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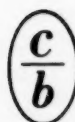
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## STUDY OF THE REACTIONS INVOLVED IN THE FORMATION OF COBALT AND NICKEL FERRITES. II.

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In a previous investigation<sup>1</sup>, there was presented a study of ferrite formation with different ratios of ferric oxide to metal suboxides. The purpose of the investigation was to establish the nature of the phase formed upon prolonged heating of the oxide mixtures. In the investigation there appeared methods for measuring the magnetic properties of the heated mixtures as well as their X-ray phase analysis.

Results of magnetic investigations carried out by Veil<sup>2</sup> for the mixtures  $\text{CoO} - \text{Fe}_2\text{O}_3$ ,  $\text{NiO} - \text{Fe}_2\text{O}_3$ , and  $\text{CuO} - \text{Fe}_2\text{O}_3$  are given on Figure 1, in which the relationship of the coefficient of magnetization to the molar composition of the mixture is presented. (Calculated by us from the weight composition, given by Veil.) The positions of the maxima correspond to equimolar compounds and indicate the presence of solid solutions.

By an analogous method Hilpert and Wille<sup>3</sup> concluded the existence of the ferrites  $2\text{CuO} \cdot 3\text{Fe}_2\text{O}_3$  and  $2\text{FeO} \cdot 3\text{Fe}_2\text{O}_3$ , which, however, is not confirmed by X-ray phase investigations; the latter indicating only two phases in the presence of excess  $\text{Fe}_2\text{O}_3$ : spinel (cupric or magnetic) and hematite.

The magnetic and X-ray phase analysis of the heated mixtures  $\text{NiO} - \text{Fe}_2\text{O}_3$  and  $\text{CuO} - \text{Fe}_2\text{O}_3$  was carried out by van-Arkel, Verwey and van-Bruggen<sup>4</sup>, who found that the ferric oxide, occurring in large quantities in the spinel lattice, corresponding to the lattice  $\gamma - \text{Fe}_2\text{O}_3$  and forming solid solutions with wide concentration intervals, does not change the parameters of the spinel lattice and therefore is not discernible roentgenographically.

Table 1 presents a summary of the results of van-Arkel et al. It is here evident that from 1000-1100°C the homogeneous ferrite region is extended to 60% (mol) of  $\text{Fe}_2\text{O}_3$ , the boundaries of the region sharply changing with temperature. Van-Arkel considers that the solution of  $\gamma - \text{Fe}_2\text{O}_3$  in the copper lattice increases its magnetic properties, and therefore the maximum magnetization occurs at 60%  $\text{Fe}_2\text{O}_3$ , as was found by Hilpert; but from which it cannot be concluded that the stoichiometric compound  $2\text{CuO} \cdot 3\text{Fe}_2\text{O}_3$  exists.

By cooling solid solutions of  $\text{Fe}_2\text{O}_3$  in ferrite sufficiently slowly, a decomposition of the solutions occurs with separation of the excess  $\text{Fe}_2\text{O}_3$  as hematite.

Excess  $\text{NiO}$  is also soluble in  $\text{NiO} \cdot \text{Fe}_2\text{O}_3$ , and since the  $\text{NiO}$  lattice (as also the  $\text{MgO}$ ) is identical with the spinel lattice, and the unit cell is twice as small, the roentgenographic detection of solid solutions can only be done indirectly. These solutions decompose at 1000°C, and at 900°C the solubility of  $\text{NiO}$  in  $\text{NiO} \cdot \text{Fe}_2\text{O}_3$  is apparently very small.

Since various conclusions on solid solutions can be drawn from the data for  $\text{NiO} \cdot \text{Fe}_2\text{O}_3$  given by van Arkel, and since an X-ray phase analysis for  $\text{CoO} \cdot \text{Fe}_2\text{O}_3$  was not carried out, we proposed to supplement the investigation with the process for the formation of cobalt and nickel ferrites in equimolecular mixtures, as well as magnetic and X-ray phase investigations.

TABLE I

Roentgenographic investigation of the system  $\text{NiO-Fe}_2\text{O}_3$  and  $\text{CuO-Fe}_2\text{O}_3$   
(according to van-Arkel, Verwey and van Bruggen)

MeO	Heating time (in hours)	Temperature	Molecular % in the mixture										
			Fe <sub>2</sub> O <sub>3</sub>	40	45	50	55	60	65	70	75		
			MeO	60	55	50	45	40	35	30	25		
NiO	8	1300°C		Ferrite									
	3.5	1050											
	4	900											
				Ferrite and Hematite									
CuO	3	1250		Ferrite									
	40	1080											
	4	900											
	4	750											
				Ferrite and Hematite									

of the final products of the reaction of  $\text{CoO}$  and  $\text{NiO}$  with  $\text{Fe}_2\text{O}_3$  in mixtures of various compositions.

The mixtures of  $\text{CoO-Fe}_2\text{O}_3$  and  $\text{NiO-Fe}_2\text{O}_3$  were prepared by the combined grinding and sieving of the pure dry oxides (see <sup>1</sup>). The composition of the mixtures differed from the proposed molecular ratio, rounded off, by less than 0.1% and only in two cases by 0.15 - 0.2%.

According to our investigations <sup>1</sup>), the time necessary for the practical completion of ferritization in equimolar mixtures at 1100°C is 25-30 hours. Supplementary experiments on heating mixtures with various ratios of  $\text{MeO}$  and  $\text{Fe}_2\text{O}_3$  for 30 and 40 hours indicated that the magnetic effect is not noticeably increased after 30 hours, and in several cases decreases somewhat by amounts which could not be measured accurately.

Thus, the mixture was heated 30 hours, cooled by removing the quartz vessel from the furnace, i.e., quite rapidly, screened through a 0.1 mm. sieve and subjected to magnetic measurements, the method for which see <sup>1</sup>). The magnetic effect obtained was then referred to 0.01 mols of the mixture, the molecular weight of which varied from one mixture to another.

The results of the measurements are shown in Table 2. The corresponding curve is given in Diagram 2. The data obtained indicate the small solubility of  $\text{MeO}$  in spinel. The maximum magnetization is directed toward the side of  $\text{Fe}_2\text{O}_3$  and corresponds to the composition  $\text{NiO} \cdot 2\text{Fe}_2\text{O}_3$ . A special feature of the diagram obtained is the sharp drop of the curve at the  $\text{Fe}_2\text{O}_3$  portion with the formation of concave curves, which do not appear on Veffl's diagrams and concerning which nothing is mentioned in the work of van Arkel. A solution of  $\text{Fe}_2\text{O}_3$  in cobaltic spinel is not observed according to data indicated in the magnetic measurements. X-ray phase analyses were also carried out as before <sup>1</sup>) and the results presented in Tables 3 and 4.

In all the roentgenograms spinel lattices are found. The  $\text{CoO-Fe}_2\text{O}_3$  lattice is constant at 8.36 - 8.37 Å and is characterized by us as a spinel-Co. According to the literature, this lattice varies from 8.32 - 8.47 Å. In accordance with van Arkel's results we observed neither a regular nor a generally existing variation in the lattice constant with variation in composition of the mixture in mixtures with excess  $\text{Fe}_2\text{O}_3$ , although in several mixtures (Nos. 2 and 4, for example) different in composition, the spinel occurred as a single phase.

In mixtures with an excess  $\text{CoO}$ , where the latter is present as an individual phase, the spinel lattice has another value (8.343 - 8.335 Å), evidently corresponding to a spinel saturated with cobalt suboxide. We are defining this phase as a spinel-Co<sup>1</sup>.

Table 2

Magnetic variations of the systems  $\text{CoO} - \text{Fe}_2\text{O}_3$  and  $\text{NiO} - \text{Fe}_2\text{O}_3$ 

Original composition of the mixture	Average molecular wt. of mixture	Average molecular wt. of mixture		Weight of the powder	Deflection of the galvanometer (in mm)	Deflection for 1 gm. powder	Magnetic effect	
		CoO	$\text{Fe}_2\text{O}_3$				for 1 gm. of the powder	for 0.01 g. of the average molecular wt. of the mixture
$\text{CoO}:4\text{Fe}_2\text{O}_3$ . . . . .	143	20.0	80.0	2.5485	10.0	3.9	5.6	8.0
$\text{CoO}:2\text{Fe}_2\text{O}_3$ . . . . .	132	33.3	66.7	2.1690	6.5	3.0	4:3	5.7
$2\text{CoO}:3\text{Fe}_2\text{O}_3$ . . . . .	126	40.0	60.0	2.4908	19.5	7.8	11.3	14.2
$\text{CoO}:\text{Fe}_2\text{O}_3$ . . . . .	117	50.0	50.0	2.3581	97.5	41.4	59.8	70.0
$2.75\text{CoO}:2.25\text{Fe}_2\text{O}_3$ . . . . .	113	55.0	45.0	2.3712	97.0	40.0	59.2	66.9
$3\text{CoO}:2\text{Fe}_2\text{O}_3$ . . . . .	109	60.0	40.0	2.6569	106.0	39.9	57.7	62.9
$2\text{CoO}:\text{Fe}_2\text{O}_3$ . . . . .	103	66.7	33.3	2.6915	86.5	32.1	46.5	47.9
<hr/>								
		Average molecular wt. of mixture						
		NiO	$\text{Fe}_2\text{O}_3$					
$\text{NiO}:9\text{Fe}_2\text{O}_3$ . . . . .	151	10.0	90.0	2.4754	13.5	5.4	7.8	11.8
$\text{NiO}:4\text{Fe}_2\text{O}_3$ . . . . .	143	20.0	80.0	2.4956	35.5	14.2	20.6	29.5
$\text{NiO}:2\text{Fe}_2\text{O}_3$ . . . . .	131	33.3	66.7	2.0990	74.0	35.3	51.1	69.9
$2\text{NiO}:3\text{Fe}_2\text{O}_3$ . . . . .	126	40.0	60.0	2.0282	72.5	35.8	51.8	65.3
$\text{NiO}:\text{Fe}_2\text{O}_3$ . . . . .	117	50.0	50.0	2.5352	87.5	34.5	49.9	58.4
$2\text{NiO}:\text{Fe}_2\text{O}_3$ . . . . .	103	66.7	33.3	2.7038	69.0	25.5	36.9	33.0

Table 3

X-ray phase analysis of the system  $\text{CoO} - \text{Fe}_2\text{O}_3$ 

Series	Original composition of the mixture	Molar percent in the mixture		Roentgenograms		
		CoO	$\text{Fe}_2\text{O}_3$	lg a	a lattice constant ( $\text{\AA}$ )	Phase composition of the mixture
17	$\text{CoO}:4\text{Fe}_2\text{O}_3$ . . . . .	20.0	80.0	--	--	
16 bis	$\text{CoO}:2\text{Fe}_2\text{O}_3$ . . . . .	33.3	66.7	0.9224	8.364	Spinel-Co
19	$2\text{CoO}:3\text{Fe}_2\text{O}_3$ . . . . .	40.0	60.0	0.9225	8.366	Spinel-Co hematite (much)
13 bis	$\text{CoO}:\text{Fe}_2\text{O}_3$ . . . . .	50.0	50.0	0.9226	8.368	Spinel-Co
20	$2.75\text{CoO}:2.25\text{Fe}_2\text{O}_3$ . . . . .	55.0	45.0	0.9224	8.364	Spinel-Co hematite (traces)
18	$2\text{CoO}:3\text{Fe}_2\text{O}_3$ . . . . .	60.0	40.0	0.9213	8.343	x-phase (very small) Spinel-Co', x-phase (very small) CoO
15	$2\text{CoO}:\text{Fe}_2\text{O}_3$ . . . . .	66.7	33.3	0.9209	8.335	Spinel-Co', hematite (traces) CoO

The lattice constant for nickel spinel does not vary in all the concentrations studied (8.321 - 8.331 Å). The data in the literature show - 8.32 - 8.41 Å.

Besides spinels, the existence of other, unknown phases, were observed: traces of x-phases in cobalt mixtures with excess CoO and large quantities of y-phases in nickel mixtures with traces of  $\text{Fe}_2\text{O}_3$ . Up to now we have not figured out the structure of these phases. Without examining the x-phase, which appears in small quantities, we may consider the y-phase, which is present in large quantities in mixtures of 80 - 90%  $\text{Fe}_2\text{O}_3$ , as ferrite with the formula  $\text{NiO} \cdot n\text{Fe}_2\text{O}_3$ , with a crystalline structure different from a spinel and not possessing ferromagnetism. Probably this phase appears as a decomposition product when solid solutions of  $\text{Fe}_2\text{O}_3$  in spinel are subjected to prolonged heating (the drop in magnetism in mixtures heated over 30 hours has been discussed).

Table 4  
X-ray phase analysis of the system  $\text{NiO} - \text{Fe}_2\text{O}_3$

Series	Original composition of the mixture	Molar percent in the mixture		Roentgenograms		
		CoO	$\text{Fe}_2\text{O}_3$	lg a	a lattice constant (Å)	Phase composition of the mixture
19	$\text{NiO} : 9\text{Fe}_2\text{O}_3$ . . . . .	10.0	90.0	0.9207	8.331	Spinel-Ni hematite (much) y-phase (much)
17	$\text{NiO} : 4\text{Fe}_2\text{O}_3$ . . . . .	20.0	80.0	0.9204	8.325	Spinel-Ni hematite (much) y-phase (much)
16 bis	$\text{NiO} : 2\text{Fe}_2\text{O}_3$ . . . . .	33.3	66.7	0.9208	8.333	Spinel-Ni hematite y-phase (small)
18	$2\text{NiO} : 3\text{Fe}_2\text{O}_3$ . . . . .	40.0	60.0	0.9202	8.321	Spinel-Ni hematite y-phase (small)
13	$\text{NiO} : \text{Fe}_2\text{O}_3$ . . . . .	50.0	50.0	0.9200	8.318	Spinel-Ni
15	$2\text{NiO} : \text{Fe}_2\text{O}_3$ . . . . .	66.7	33.3	0.9203	8.321	Spinel-Ni, NiO (much)

The same considerations may be used to explain the straight portion of the curve for the magnetic properties of  $\text{CoO} - \text{Fe}_2\text{O}_3$ , although new phases are not formed here; ferric oxide not even forming in mixtures of 67%  $\text{Fe}_2\text{O}_3$ . If this fact is not considered and it is assumed that in a mixture of 60%  $\text{Fe}_2\text{O}_3$ , i.e. in composition situated close to spinel, a large quantity of  $\text{Fe}_2\text{O}_3$  is found, then it can be proposed that if solid solutions of  $\text{Fe}_2\text{O}_3 - \text{CoO} \cdot \text{Fe}_2\text{O}_3$  are formed (which is indirectly indicated by Veil's data), they decompose upon heating with the formation of a new phase  $\text{CoO} \cdot n\text{Fe}_2\text{O}_3$ , where  $n = 1.5 - 2$ ; this phase, evidently, cannot be differentiated from hematite, but not being ferromagnetic, it causes a sharper decrease in the magnetization of mixtures to the right of the maximum in comparison with stoichiometric spinel.

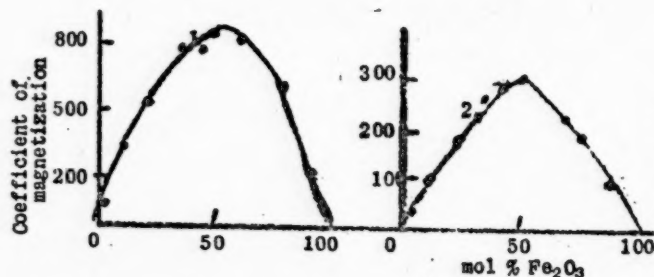


Fig. 1. Magnetic analysis of the systems  $\text{NiO} - \text{Fe}_2\text{O}_3$  and  $\text{CoO} - \text{Fe}_2\text{O}_3$ , according to Veil.  
1:  $\text{NiO} - \text{Fe}_2\text{O}_3$  2:  $\text{CoO} - \text{Fe}_2\text{O}_3$

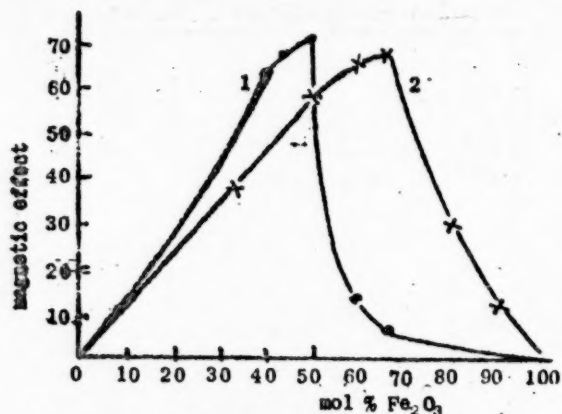


Fig. 2. Magnetic analysis of the system  $\text{CoO} - \text{Fe}_2\text{O}_3$ . 1- $\text{CoO} - \text{Fe}_2\text{O}_3$ . 2- $\text{NiO} - \text{Fe}_2\text{O}_3$ .



In Hilpert's works <sup>3,5</sup>, concerning the crystalline structure of ferrites, a whole series of compounds are shown, rich in  $\text{Fe}_2\text{O}_3$  and possessing a hematite lattice. These are:  $\text{CuO} \cdot n\text{Fe}_2\text{O}_3$ ,  $2\text{MnO} \cdot 3\text{Fe}_2\text{O}_3$ ,  $\text{FeO} \cdot n\text{Fe}_2\text{O}_3$  where  $n > 3$ , aluminum ferrites, etc.

This preliminary description of phase transformations in the systems studied should be confirmed and made more accurate by further investigations, in which it would be necessary, however, to raise the temperature in order to shorten the heating time, and make a detailed study of the time factor:

#### CONCLUSIONS

1. Magnetic properties and phase compositions were investigated in mixtures of  $\text{CoO} + n\text{Fe}_2\text{O}_3$  and  $\text{NiO} + n\text{Fe}_2\text{O}_3$ , heated at  $1100^\circ\text{C}$  for 30 hours.

2. Little solubility was observed at this temperature for  $\text{CoO}$  and  $\text{NiO}$  in the spinels  $\text{MeO} \cdot \text{Fe}_2\text{O}_3$ .

3. Considerable solubility of  $\text{Fe}_2\text{O}_3$  in  $\text{NiO} \cdot \text{Fe}_2\text{O}_3$  was observed. This was associated with an increase of the magnetic properties up to the maximum for  $\text{NiO} \cdot \text{Fe}_2\text{O}_3$ , analogous to the copper and iron ferrites studied by Hilpert.

A sharp drop was found in the magnetic properties of mixtures richer in  $\text{Fe}_2\text{O}_3$  than  $\text{NiO} \cdot 2\text{Fe}_2\text{O}_3$  and  $\text{CoO} \cdot \text{Fe}_2\text{O}_3$ . In the first system the appearance of an unknown phase  $\gamma$  was noted, which is probably a nickel ferrite with a high  $\text{Fe}_2\text{O}_3$  content, not possessing ferromagnetism. In the system  $\text{CoO} - \text{Fe}_2\text{O}_3$  the drop in magnetic properties is still sharper and could be similarly explained but for the fact that the cobalt ferrite is evidently identical to hematite in structure and cannot be differentiated, roentgenographically, from the latter.

5. The formation of ferrites, rich in ferric oxide, takes place slowly at  $1100^\circ\text{C}$ , possibly because of the decomposition of the solid solutions  $\text{CoO} \cdot \text{Fe}_2\text{O}_3 - \text{Fe}_2\text{O}_3$  and  $\text{NiO} \cdot \text{Fe}_2\text{O}_3 - \text{Fe}_2\text{O}_3$ , and was therefore not observed by van Arkel or Veil. Apparently, the speed of formation of ferrite, rich in  $\text{Fe}_2\text{O}_3$ , in the system  $\text{CoO} - \text{Fe}_2\text{O}_3$  is significantly higher than in the system  $\text{NiO} - \text{Fe}_2\text{O}_3$ .

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## KINETICS OF THE REACTION OF MERCURY VAPORS WITH OZONE

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In one of our previous works [1] data were obtained on the formation and protective properties of films formed on the surface of mercury, at usual temperatures, by treating it with chlorine or ozone in small concentrations.

In the present work, we proposed to study these reactions, only substituting mercury vapor for metallic mercury.

The initial methods for these investigations differed little from the previous ones and were carried out as follows. Over metallic mercury with a surface of about 100 cm<sup>2</sup> and 200°C, pure air was passed at the linear rate of 5 l. per minute. Under these conditions the concentrations of mercury vapor was 61/g. (micrograms) in 1 l. A burette was also included in the system to measure out the gases. The solid products of the reaction were collected in a glass spiral approximately 1 M in length (See below). The residual mercury vapor was collected in another such spiral, in the beginning of which was placed a crystal of iodine. The mercuric iodide thus obtained was dissolved in a 0.5% solution of potassium iodide, and the mercury content determined colorimetrically as the mercury sulfide.

Experiments indicated that in the reaction of mercury vapor with chlorine at usual temperatures, there occurred a quantitative combination of mercury with an amount of chlorine less than that required by the stoichiometric relationship for mercuric chloride. It had to be assumed that the principal formation, here, was not mercuric, but mercurous chloride.

Upon treating the white precipitate deposited in the first spiral with warm water and analysis of the solution obtained after filtering the insoluble precipitate, only very small quantities of mercury were found. Therefore, the major portion of mercury was combined with the chlorine as Hg<sub>2</sub>Cl<sub>2</sub>.

Special experiments were conducted for the purpose of establishing the relationship of divalent to monovalent mercury, dependent on the concentration of chlorine. The data for these experiments are shown in Table 1.

As shown in Table 1, a very large increase in the chlorine concentration has a comparatively small influence on the yield of divalent mercury.

In as much as the reaction of mercury vapor with chlorine takes place with such great speed, it was necessary for us to give up our planned study of this speed.

Analogous experiments were carried out with ozone. Knowing how quickly ozone reacts with

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The term 'monovalent' mercury and the corresponding designation in the table, we here use conditionally

Table 1  
Variations in the yield of divalent mercury with chlorine concentration, for combinations of mercury vapor with chlorine.

Cl Hg	$\frac{\text{Hg}^{++}}{\text{Hg}^{+} + \text{Hg}^{++}} \cdot 100$
2	7.3
4	12.3
8	19.0
16	II 28.6



metallic mercury, we had every basis to believe that the reaction of mercury vapor with ozone would also take place with a fairly great speed, at usual temperatures. Preliminary experiments showed, however, that this speed of reaction was small compared with the reaction with halogens.

Reactions between mercury vapor and ozone were first observed by Manchot and Kampschulte[2]. Upon treating metallic mercury with ozonized oxygen containing 1.5% ozone, a brownish-yellow deposit of mercuric oxide appeared on the walls of the reaction tube at 55°C, and at 120°C a rapidly forming light-brown vapor was observed, the color of which intensified with increasing temperature. Nothing is described in the literature concerning the reaction of mercury vapor with ozone at usual temperatures using small concentrations of the reacting substances.

Since our ultimate purpose was to study the speed of the given reaction, we considered it necessary to first obtain orientating data, on the basis of which we would be able to devise a method to effect a more thorough investigation of the problem.

Table 2  
Variation in speed of reaction of mercury vapor and ozone with concentration

$\frac{O_3}{Hg}$	Amount of mercury oxidized by ozone (in % of total quantity)
2	Traces
4	26.0
8	68.4
16	92.4
32	100.0

Table 3  
Action of mercury vapor with ozone in the presence of a catalyst

$\frac{O_3}{Hg}$	length of time for the experiment (in hours)	Amount of mercury oxidized by ozone (in % of total quantity)
2	1	94.7
2*	4	93.6
2	8	91.5
4	3	100.0

The purpose of the first experiments was to establish the relationship of the quantity of mercury combined with ozone with its concentration. The conditions of the experiment are similar to those of the reaction of mercury vapor and chlorine. Each experiment lasted 30 minutes. The amount of mercury oxidized by the ozone was determined by dissolving the mercury oxide deposited in the first spiral in potassium iodide and then determining mercury sulfide colorimetrically. By an analogous method, the remaining mercury was determined, precipitated as the mercuric iodide in the second spiral. The experimental data are shown in Table 2.

Table 2 indicates that the speed of reaction of mercury vapor with ozone is not great, especially when compared with the reaction of mercury vapor with chlorine, where a quantitative combination of mercury occurs with small concentrations of chlorine.

Analogous experiments were carried out with ozone in the presence of a catalyst - activated carbon, with a layer 1 cm. in height and a surface area of 1 cm<sup>2</sup>, placed in a special glass tube and inserted before the spiral with the iodine crystal.

Under the conditions of the experiment, the mercuric oxide formed by the ozone oxidation was completely precipitated on the surface of the activated carbon, and the remaining mercury was precipitated in the iodine-bearing spiral. The experimental data are shown in Table 3.

Upon comparing the data in Tables 2 and 3 it can be stated that the speed of reaction of mercury vapor with ozone is sharply increased in the presence of activated carbon. With twice as much ozone as mercury, without the catalyst, only traces of mercuric oxide was found, but in the presence of the catalyst 75% is oxidized. In this respect it is necessary to note that the activity of the catalyst slowly decreases due to the coating of mercuric oxide on the active surface. After 8 hours of the experiment, about 15 mg. of mercuric oxide was deposited on the surface of the carbon (weight 1.2 gm.) and the activity of the catalyst decreased by 3%.

Finally, the last of these groups of experiments was conducted for the purpose of studying the relationship of the speed of reaction to temperature. The data is shown in Table 4' (the curve on Fig. 1).

The following group of experiments was conducted with the purpose of studying the speed of reaction of ozone and mercury vapor under static conditions and in such a manner as to subject the data obtained to mathematical computation. It was necessary to place the mercury and ozone, in known concentrations, in covered reservoirs, and in definite intervals of time, to determine the amount of unreacted mercury. Calculation by means of the remaining ozone was not possible in view of its instability.

Taking into consideration that the reaction vessel is to be placed in a thermostat, its volume should be limited to a maximum of about 10 l. In this connection it would be necessary to choose a method of analyzing the mercury vapor which would be sufficiently sensitive and possess high accuracy. From our point of view such requirements were satisfied by the dithizone method for determining small quantities of mercury, first proposed by Fischer and Leopoldi [3] and somewhat modified by Kuziatkin [4] for analysis of air containing mercury vapor. Essentially, the method calls for the extraction of mercury from an aqueous solution by means of a solution of dithizone in chloroform or carbon tetrachloride, in which the green dithizone color is gradually changed to the orange mercury dithizonate. The mercury content is determined colorimetrically by the duplication method. After carefully testing this method we came to the conclusion that completely satisfactory accuracy could only be achieved if the extraction is carried out at all times to an obvious rose color - with a solution of dithizone containing an excess of mercury. If the test solution contains a small quantity of mercury, the final addition of dithizone can be brought to a rose color by addition of a standard solution of a mercury salt with a known titer. Essentially, this modification of the method will not be colorimetric but titrimetric, with the possibility of using back-titrations. The most accurate results were obtained with dithizone having an optimum titer of 1.5 - 2  $\mu$  g. of mercury. In Table 5 is presented data which verify this method.

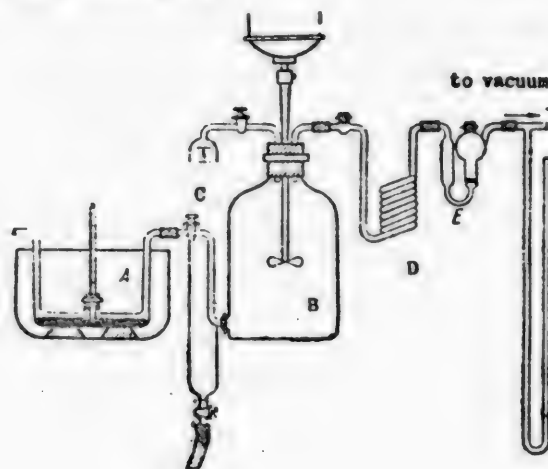


FIG. 2. Apparatus for studying the kinetic reaction of mercury vapor with ozone

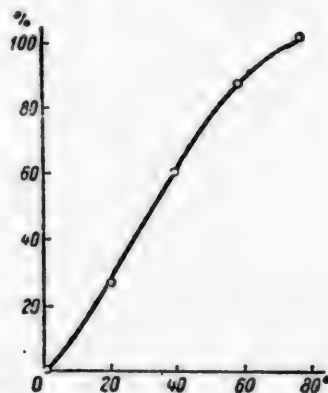


Fig. 1 Increase of speed of reaction with temperature for mercury vapor and ozone.

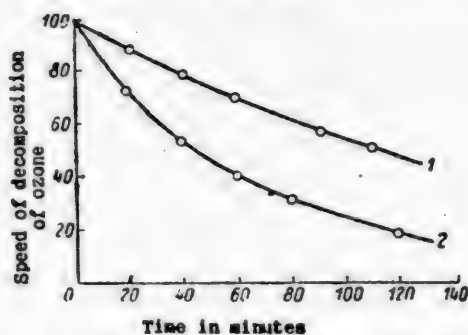


Fig. 3. Speed of decomposition of ozone.  
1) decomp. of ozone in dispensing burette  
2) decomp. of ozone in reaction vessel.

In our investigations it was necessary for us to determine, for the most part, absolute quantities of mercury, not less than 5 $\mu$ g. As is shown in Table 5, in such cases the experimental error is not over 5%. For the given quantities of mercury, hardly any other method could give greater accuracy.

The apparatus in which we conducted our investigations is shown in Fig. 2.

Table 4  
Variation of speed of reaction with temperature for  
mercury vapor and ozone

$\frac{O_3}{Hg}$	Temperature	Amount of mercury oxidized by ozone (in % of total quantity)
4	20°C	26.0
4	40	59.6
4	60	86.5
4	80	100.0

Table 5  
Results to verify the dithizone method  
for determining small quantities of  
mercury

Mercury present (in $\mu$ g.)	Mercury found (in $\mu$ g.)
1.0	1.1
2.0	2.1
5.0	5.0
10.0	10.5
15.0	14.8
20.0	19.8

The bucket with metallic mercury A, placed in the thermostat, served to dispense the mercury. Air containing mercury vapor at 20°C was passed through reservoir B, volume 5.6 l., situated in a thermostat (not shown in Fig. 2) at the rate of 1 l. per minute for 30 minutes. From the burette C, volume 700 ml., a definite volume of ozonized air with a known concentration of ozone was passed into the reservoir, the time noted and, after 10 seconds, the agitation begun.

Also, during the course of the operation, a definite volume of ozonized air was slowly passed into the reservoir from the burette in order to compensate for the ozone which was decomposed during the course of the experiment. In as much as the volume of ozonized air added was not large, we surmised that the agitation used produced an adequate diffusion.

To calculate this supplementary volume of ozonized air, we conducted special investigations on the speed of decomposition of ozone under the conditions of our experiment. The results of these investigations are shown in Fig. 3. The concentration by volume of ozone in the burette was on the average 0.03% and in the reservoir approximately 10 times less. In spite of what the curve indicates, the ozone was decomposed much faster in the reservoir than in the burette.

The air in the burette, situated above water, naturally has a higher moisture content than the air in the reservoir. It is known that the presence of moisture retards the decomposition of ozone. Besides, the presence of rubber stoppers in the reservoir also causes some additional decomposition of the ozone.

In a definite length of time after the reaction had started, the stopcock was closed, and the shaft of the agitator was lowered in order to seal the top, wider portion of the opening in the rubber stopper used in the reservoir. The air in the reservoir was evacuated to  $\frac{1}{2}$  an atmosphere, the remaining mercury being absorbed in the micro-absorbent D, containing a solution of 0.1 N permanganate, acidified with sulfuric acid. In special preliminary experiments without the addition of ozone, it was established that under these conditions actually half of the total quantity of mercury was quantitatively absorbed by the permanganate. The spiral E served to retain the mercuric oxide that was not deposited in the reaction vessel. The excess permanganate in the absorbent was combined with a minimum excess of oxalic acid. The volume of the solution was adjusted to 10 ml. and added from a micro-burette to 1 ml. of a solution of dithizone in chloroform, with careful shaking until a permanent orange color was obtained. The standard solution of mercury for establishing the titer of the dithizone was prepared from doubly recrystal-

lized mercuric chloride in the presence of those ingredients found in the standard solution.

The surface area in the bucket was approximately 70 cm<sup>2</sup>. At a constant temperature of 20°C and a constant rate of flow of air over the metallic mercury of 250 ml. for each 1 cm<sup>2</sup> cross-section of the bucket, the concentration of the mercury vapor in the reaction vessel was equal to 7.9 μg. for 1 l. of air, or 3.94 x 10<sup>-8</sup> g.-atoms of mercury. The concentration of ozone in all the experiments was also constant and equal to 5.4 μg. for 1 l., or 11.3 · 10<sup>-8</sup> gram-mol.

The results of the experiments are shown in Table 6.

Each experiment was repeated at least twice for a given temperature. Here, the reproducibility was fully satisfactory and the decomposition did not exceed the limits of experimental error. The average data is shown in the second graph. As is indicated in Fig. 4, this data forms a well-defined curve.

The constant was calculated according to the equation

$$K = \frac{1}{t} \cdot \frac{1}{a-b} \ln \frac{(a-x)b}{(b-x)a}$$

obtained after integration of the well-known equation for a second order reaction. The letter a signifies the concentration of ozone in gm.-mol, the letter b signifies the concentration of mercury in gm.-at., and

the letter x - the amount of mercury entering into the reaction. Taking into consideration the very small concentrations of the initial substances, concentrations for which, as far as we know, the speed of reaction has not been studied, the agreement between the experimental constants and the different durations of reactions was excellent.

The last experiments were aimed at establishing the influence of temperature upon the speed of reaction of mercury vapor with ozone. Since exploratory data concerning this was obtained in our preliminary experiments (see above), we considered it practicable to confine ourselves only to the verification of this data.

Conditions for the experiments were the same, except that instead of a mercury vapor concentration of 7.9 μg. per 1 l., a concentration of 9.1 μg. was used in obtaining the experimental data. The ozone concentration was the same.

The experiments lasted 10 minutes, at temperatures of 20 and 30°C. In the first case 1.5 μg. of mercury entered into the reaction, and in the second case 2.5 μg. of mercury - the average data from two duplicate experiments.

Consequently, upon raising the temperature 10°C, the speed of the reaction increases 1.66 times. At this temperature interval, the figure obtained for the previous experiments was 1.73 (see curve, Fig. 1.

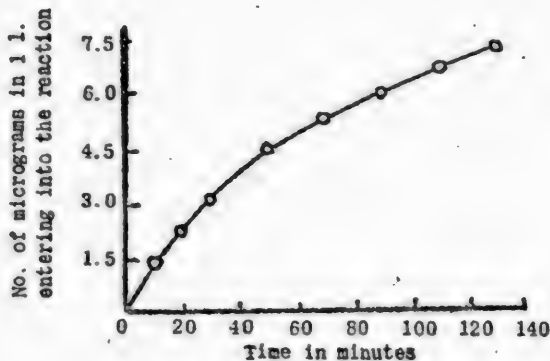


Fig. 4. Speed of reaction of mercury vapor with ozone.

Table 6  
Data on the speed of reaction of mercury vapor with ozone

Duration of experiment in minutes	Amount of reacted mercury in μg./l	K
10	1.32	0.00032
20	2.37	0.00033
30	3.20	0.00033
40	3.95	0.00032
50	4.50	0.000325
70	5.30	0.000326
90	6.03	0.00032
110	6.55	0.00032
130	7.00	0.00035

### CONCLUSIONS

1. Experiments were carried out to test the accuracy of the dithizone method for determining small quantities of mercury.
2. Preliminary experiments were conducted, characterizing the speed of reactions of mercury vapor with chlorine and ozone.
3. In the former case, the reaction proceeds with great rapidity, a mixture of mercuric and mercurous chloride being obtained, where the quantity of the latter slowly increases with increasing concentration of chlorine.
4. The reaction of mercury vapor with ozone proceeds still more slowly. By special experiments it was established that the constant of this velocity, calculated from the equation of a second order reaction, is equal to 0.000325.
5. Upon raising the temperature 10° in the limits from 20 to 30°C, the speed of reaction increases 1.7 times.

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## OXIDATION AND EVAPORATION OF MERCURY DROPLETS

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In one of our previous works [1], we studied the oxidation of mercury droplets in air in relation to the decrease in its rate of evaporation. In that investigation, however, the question of how the size of the mercury droplet influences the rate of formation of a protective oxide film was not completely covered; nor was the related subject, the influence of variations in temperature upon the rate of mercury evaporation.

We considered it expedient to conduct a series of experiments to study the relation of the rate of evaporation of mercury to the size of the drop under dynamic conditions.

Although the question of evaporation of liquids under static conditions has been completely and satisfactorily covered in the literature, thus far an absolute theory of dynamic evaporation has not; especially as related to the droplet condition.

The mercury which we used for the experiments was first purified anodically and then doubly distilled, the first time under vacuum and the second time at atmospheric pressure. According to Tereschenko [2], the second method of purification was more efficient, in as much as in this case a complete oxidation of the contaminating metals by the atmospheric oxygen takes place, which at the same time excludes the possibility of contaminating the distillate with these metals. We should state, however, that no difference in the oxidation of mercury by air was observed between a single distillation under vacuum and a supplementary distillation at atmospheric pressure.

For the preparation of a large quantity of drops of equal diameter, we prepared a capillary, the cross-sectional diameter of which was 0.15 mm. in the lowest portion and towards the top gradually increased to a diameter of 0.4 mm. Another, approximately similar capillary was attached to this capillary by means of a small section of elastic rubber tubing. The mercury, drawn up in the lower capillary, is slowly dropped, while the end of the capillary is submerged in the mercury. Upon removing the capillary from the mercury, the lowering of the mercury ceases. In this fashion, it was possible to obtain a column of mercury of any desired height. Using this system, we calibrated the capillary for drops of mercury with radii from 0.22 to 0.85 mm.

A group of droplets of a given radius was prepared on a glass slide in a current of carbon dioxide gas. The amount varied from 11 for the largest to 132 for the smallest. The preparation was placed in a glass tube and a stream of air passed through it at a rate of 250 ml. for each 1 cm<sup>2</sup> cross-section of the tube.

The tests on the rate of evaporation over fresh surfaces usually lasted 5 minutes and over oxidized mercury took a much longer time.

The results of the first experiments are shown in Table 1.

Independent of the number of drops in the investigated preparations, the surfaces in all the experiments was calculated for the average quantity - 66 drops.

For calculation of the total surface, we considered that the drops of mercury were truncated where they came into contact with the glass. The radius of these segments for the various drops,



was 2/3 the radius of the drops, from which the corresponding formula of the spherical surface of a segment was calculated to be equal to 1/12 of the total area of the drop. The total surface of the drop, calculated from its weight, was decreased by this magnitude.

As is evident from Fig. 1, the rate of evaporation from an equal quantity of drops has a linear relation to the radius of the drops. Only where the largest drops were concerned, did the rate of evaporation not fall on straight lines. This is probably explained by the flatter formation of these drops. As is known, the surface of a spheroid is greater than the surface of a sphere of the same mass.

The linear relation of the rate of evaporation of a drop to its radius was expressed by Maxwell [3] by the following equation:

$$W = 4\pi Da c_0,$$

where  $W$  is the amount of liquid evaporated in unit time,  $D$  is the coefficient of diffusion,  $a$  is the radius of the drop and  $c_0$  is the concentration of the saturated vapor at the surface of the drop.

The Maxwell equation characterized the evaporation of drops under static conditions. Our experiments show that under dynamic conditions, a linear relationship also exists between the rate of evaporation of a drop and its radius.

Appropriately, we will here compare the results of our investigations on the evaporation of a drop of mercury with the investigations of Ljalikov [4], which was concerned with the same question, but for a different purpose and by a different method. The author's aim was to verify experimentally the equation of Thompson, somewhat modified by Helmholtz:

$$\frac{KT}{M} \ln \frac{P_r}{P_{\infty}} = \frac{2\sigma}{\delta_f r},$$

where  $P_{\infty}$  - is the vapor tension near the plane surface,  $P_r$  - the vapor tension near the drop with the radius  $r$ ,  $\sigma$  - the surface tension, and  $\delta_f$  - the density of the liquid.

Applying a static method for the determination of the vapor pressure of small drops with a radius of 0.5 - 5  $\mu$ , the author came to the conclusion that the vapor pressure of drops with a radius of 0.5 - 2  $\mu$  obeys the Thompson equation. For larger drops the rate of evaporation was too low to be measured accurately and therefore considerable deviations were observed in these cases.

The static method is essentially a distillation of mercury under vacuum with the formation of a great many small drops.

By a mathematical transformation, the author derives the following equation from Thompson's equation:

$$V_r = - \frac{kYP_{\infty}}{r}$$

where  $V_r$  - is the rate of evaporation in gm./cm<sup>2</sup> sec.,  $Y = \frac{2\sigma M}{RT\delta_f}$  and  $k = \frac{1}{\sqrt{2\pi R}} \sqrt{\frac{M}{T}}$ .

Plotting  $\frac{1}{r}$  on the abscissa, and the rate of evaporation on the ordinate, the author found, for the most part, a linear relationship.

Several results of our investigations, modified for comparison with Ljalikov's data, are presented in Table 2.

As seen from Fig. 2, the rate of evaporation of mercury drops with unit surface in unit time has an inverse linear relationship with the radii of the drops.

Therefore, summarizing all of the foregoing, it may be considered that this relationship exists with dynamic as well as static evaporations for drops of various diameters.

Table 1

Relation of the speed of evaporation of drops to their radii

r in mm	S in mm <sup>2</sup>	Rate of evaporation	
		in $\mu\text{g}/\text{min}$ at 20°C	in $\mu\text{g}/\text{min}$ at 40°C
0.22	37.8	1.04	5.4
0.31	73.3	1.51	8.0
0.47	168.7	2.52	12.8
0.69	389.0	3.76	18.3
0.85	557.0	5.7	26.7

Table 2

Relation of rate of evaporation of drops with unit surface to their radii

$\frac{1}{r}$	Rate of evaporation in $\mu\text{g}/\text{cm}^2 \cdot \text{min}$			
	Observed at 20°	Calculated at 40°	Observed at 20°	Calculated at 40°
1.17	0.97	0.83	4.9	4.1
1.45	1.02	1.0	5.6	5.2
2.13	1.56	1.5	8.0	7.5
3.23	2.06	2.2	11.2	11.2
4.55	2.9	3.1	15.0	15.8

Table 3

Change in rate of evaporation of mercury droplets by oxidizing them in air

Length of the experiment in hours	Rate of evaporation (in $\mu\text{g}/\text{dm}^2 \cdot \text{min.}$ )			
	Drops (r = 0.22 mm)		Drops (r = 0.47 mm)	
	20°C	40°C	20°C	40°C
0.0	290	1500	150	800
1.0	132	486	108	320
2.0	64	412	78	254
4.0	31	322	43	216
8.0	19	274	33	200
24.0	17	180	18	180
48.0	16	135	16.5	137
96.0	12	96	12.0	108
300.0	8	72	8.5	82
700.0	6	—	6.0	—

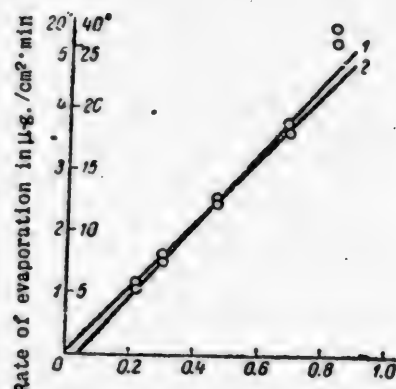


Fig. 1. Relation of the speed of evaporation of drops to their radii. 1- at 20°C. 2- at 40°C.

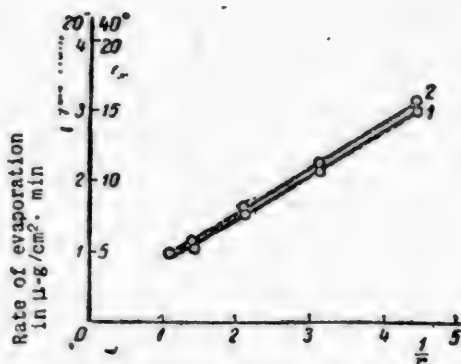


Fig. 2. Variation of rates of evaporation of drops with unit surface, with their radii 1- at 20° 2 - at 40°

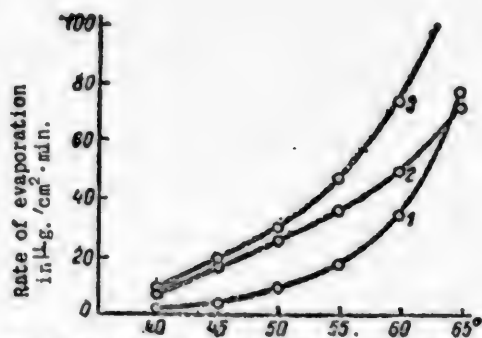


Fig. 3. Variation of the rate of evaporation with temperature of oxidized mercury surfaces. 1) Continuous mercury surfaces; 2) drops, r=0.22 mm; 3) drops, r=0.85 mm

To calculate the rate of evaporation of mercury drops in a stream of air, we propose the following formula:

$$V_r = \frac{14 \cdot P_t W^{0.86}}{r}$$

where  $V_r$  is the rate of evaporation in  $\mu\text{-g./cm}^2 \cdot \text{min.}$ ,  $P_t$  - the tension of the saturated vapor at a given temperature  $t$ ,  $W$  - the flow of air in  $\text{ml./cm}^2$  of the cross-sectional area over the surface of the mercury and  $r$  - the radius of the drop in millimeters.

As seen from Table 2, the differences between the found and calculated magnitudes do not exceed the limits of analytical error. Only for large drops with clearly defined spheroidal shapes, did the experimentally found figures exceed the calculated by 15%.

In the following experiments the influence of an oxidized film, formed by the action of atmospheric oxygen on the drops, will be studied in relation to the rate of evaporation of the drops. The experimental conditions are the same. After setting up the preparation of mercury droplets, a stream of air was passed over the test, for various intervals of time. The experimental data are shown in Table 3.

Thus, for drops with a 0.22 mm. radius, the rate of evaporation at  $20^\circ$ , after one month, approaches approximately 2% of the evaporation for fresh surfaces, and for drops with a 0.47 mm. radius - up to 4%. At  $40^\circ$  this figure will be approximately twice as large.

It is necessary to state further that the rate of evaporation from drop surfaces, sufficiently oxidized by atmospheric oxygen, does not depend upon the curvature of the surface, which is proven by the rather good agreement of the figures for the rate of evaporation of drops of different diameters, 24 hours after the beginning of the experiment.

Comparing the results of the present experiments with the results of our previous investigations on the variation of the rate of evaporation in air of mercury drops with a radius of  $2 - 3 \mu$ , it must be noted that there was a greater decrease in the evaporation rate of the latter mercury. After 10 days, the evaporation rate decreased, on the average, to 30% of the evaporation rate for fresh surfaces instead of the 3% for drops with a radius of 0.22 mm; although previously, the opposite situation was expected. At first we were inclined to explain this by an insufficient purification of the mercury in our latter experiments. However, when preparations were made from this same mercury of drops with a radius of  $2 - 3 \mu$ , it was seen that the variation of rate of evaporation in air corresponded to the data of our previous experiments.

There remained another explanation. Since before the dispersed mercury was taken for testing the rate of evaporation (the term "dispersed" is used advisedly), it was in contact with atmospheric oxygen for 1 - 2 minutes, the thought occurred to us that perhaps during this time the decrease in the rate of evaporation due to the oxide film reached a point where the further decrease in the rate took place very slowly. For drops with a radius of 0.22 mm., this limit is reached in 8 hours, and for 0.47 mm. - in 24 hours. It is not hard to imagine that only several minutes would be necessary for drops with a radius of  $2 - 3 \mu$ .

In order to verify this, we conducted the following experiment. In a cylindrical, horizontally situated glass tube, we placed a small drop of mercury and heated it in an atmosphere of pure nitrogen until it had almost completely evaporated and the drops of the condensate had settled on the walls of the tube. The test for the rate of evaporation at  $20^\circ$  was then conducted in a stream of nitrogen and afterwards in a stream of air. The difference in the amount of mercury evaporated was negligible. Even after substituting hydrogen for the nitrogen, the evaporation rate increased by only 50% in comparison with the evaporation in air; apparently because of the increased diffusion of mercury vapor in an atmosphere of hydrogen.

Therefore, the possibility of atmospheric oxygen causing the abnormal variation in the evaporation rate of diffused mercury was excluded.

It was considered quite interesting to determine the rate of evaporation of freshly

dispersed mercury of unit surface and compare it with the rate of evaporation of large drops.

To accomplish this, mercury was dispersed as a condensate on a glass slide of 12 cm<sup>2</sup> area, and the test for the rate of evaporation performed, the number of drops and their radii being calculated by microscopic examination. In Table 4 are shown the results of the calculation in one of the three investigated preparations.

Table 4

Percentage of drops of various radii in preparations of diffused mercury.

0.5 - 1 $\mu$	1 - 2 $\mu$	2 - 3 $\mu$	3 - 4 $\mu$	4 - 5 $\mu$	larger than 5 $\mu$
16	18	32	14	15	5.0

Table 5

Rate of evaporation of mercury with surfaces of different curvatures

(Evaporated (in $\mu$ - gm./dm <sup>2</sup> -min.)			
Continuous layer of mercury $s = 11$ cm <sup>2</sup>	Radius of the drops		
	from 0.5-5 $\mu$	0.22 mm	0.47 mm
18	42	290	150
After oxidation in air for 20 hours			
15.5	21.9	17.0	18.0

Thus, the average radius of the drops can be considered as 2 - 3  $\mu$ . The total surface of mercury for the preparations was 8 to 11 cm<sup>2</sup>.

Calculation yielded the following results on the rate of evaporation for 1 dm<sup>2</sup> per minute: for the first preparation - 40, for the second - 41, and for the third 45  $\mu$ -g. -- averaging 42  $\mu$ -g.. This calculation disregards the spherical surface of the segment where the drop comes into contact with the glass. In Table 5 the rate of evaporation of mercury surfaces with different curvatures is compared. In order to obtain the comparative data, special experiments were conducted on evaporation from continuous surface films of mercury under conditions identical with previous experiments.

From Table 5 it is quite evident that the greater the rate of evaporation from unit surface, the greater the decrease in the rate because of oxidation by air; also that the evaporation from oxidized surfaces of various curvatures shows little differences among themselves. If our formula, shown above, for the determination of the evaporation rate of drops with a radius of 2 - 3  $\mu$  is used, then instead of the 42  $\mu$ -g. obtained in the experiments, we would obtain 31200  $\mu$ -g., i.e. 740 times as large.

According to the investigations of McKeehan [5], drops of mercury with a radius of  $10^{-4}$  -  $10^{-3}$  cm. evaporate much slower than would be expected by Maxwell's formula, shown above. Upon evaporation under vacuum of drops with a radius of  $10^{-3}$  cm., rates of the magnitude of  $2 \cdot 10^{-7}$  g./cm<sup>2</sup>·sec. were experimentally obtained, although calculation by the formula gives  $7100 \cdot 10^{-7}$  g./cm<sup>2</sup>·sec.

Bigelow and Trimble [6] found an analogous decrease in the rate of evaporation for very small drops. Ljalikov [4] explains the anomaly of the evaporation of dispersed mercury by stating that the authors worked with insufficiently purified mercury and did not study the formation of an oxide film on the surface. Our experiments show beyond a doubt that there is some other basic reason for this phenomenon. Further experiments may throw light upon this.

Our previous investigations have established that upon treating a surface of mercury with ozone in small concentrations, the rate of evaporation of the mercury approaches zero, due to the formation of a protective oxide film upon the surface. The expression "the rate of evaporation of mercury approaches zero" was used advisedly, being "true only within the limits of sensitivity of the microscopic method used by us" [7]. The sensitivity of this accurate method did not exceed 10  $\mu$ -g..



In the present investigations, made possible by a method for determining absolute quantities of mercury down to 1  $\mu$ -g., we considered it expedient to conduct supplementary experiments to definitely establish the degree of permeability of mercury atoms through the protective oxide film, not only at ordinary temperatures, but at higher temperatures as well.

The experimental conditions were the same as described above, except that the system in which air was passed over the mercury included a burette for dispensing the ozone. The concentration of ozone was the same as in our previous investigations, i.e., 0.025 mg. per 1 liter of air passed over the mercury. Drops with radii of 0.22 and 0.85 mm. were taken for the experiment. Also, a continuous layer of mercury with a surface of 11 cm<sup>2</sup> was investigated under the same conditions.

After the ozonization of all the preparations for 15 minutes, we tested their evaporation rates at 20°C for 30 minutes.

Thereafter, under the same conditions, we tested the evaporation rates at higher temperatures. The experimental data are shown in Table 6.

Table 6

Variation of the rate of evaporation with temperature of ozonized mercury surfaces.

t°C	Evaporated (in $\mu$ -g./dm <sup>2</sup> ·min.)		
	Drops (r = 0.22 mm)	drops (r = 0.85 mm)	continuous layer (s = 11 cm <sup>2</sup> )
	up to ozonization		
20	290	100	18
20	after ozonization		
30	not detected	not detected	not detected
40	7.5	8.0	2.0
45	17.0	20.0	4.5
50	25.0	30.0	9.0
55	35.0	45.0	18.0
60	50.0	74.0	36.0
65	72.0	110.0	75.0

Thus, the oxide film possesses excellent protective properties even at higher temperatures. For small drops at 40°C only 7.5  $\mu$ -g. are evaporated, while with unoxidized surfaces under the same conditions 1500  $\mu$ -g. are evaporated (Table 2), i.e. approximately 200 times greater. Upon raising the temperature, a slow decomposition of the oxide film takes place. This is confirmed by the fact that after the ozonized droplets of mercury were subjected to an increased temperature of 50 - 60°C, they began to evaporate appreciably, even at room temperature.

It is evident from Table 6 that the greater the curvature of the surface the slower the decomposition of the film at higher temperatures. For droplets with a radius of 0.22 mm., the rate of evaporation doubled for

each 10° rise, i.e. approximately proportional to the change in vapor tension; while for the continuous layer of mercury the rate of evaporation increased 4 times for each 10° rise (Fig. 3).

Evaporation of the continuous layer of mercury from the surface at room temperature after ozonization was not detected, since the surface was too small. Additional experiments were conducted on the ozonization of surfaces 80 cm<sup>2</sup> in area. Using the same ozone concentrations, 0.025 mg./l., the ozonization lasted 30 minutes instead of the 15 minutes in the previous experiment. The rate of flow of air was 100 ml. per 1 cm<sup>2</sup> cross-section of the mercury layer. The experimental data are shown in Table 7.

The increase of the rate of evaporation was again 4 times for each 10° rise.

The figure for the evaporation of mercury

Table 7

Variation of the rate of evaporation with temperature of ozonized mercury surfaces.

t	Evaporated (in $\mu$ -g./dm <sup>2</sup> ·min.)
20°C	0.07
30	0.029
40	1.2
50	4.8
60	20.0

at 20°C = 0.07  $\mu$ -g., increases to 0.12  $\mu$ -g. if the rate of flow of air is not 100, but 250 ml. as in the previous experiment. An almost similar figure is obtained from Table 6, if the rate of evaporation in the continuous layer at 40°C is decreased 16 times (a change of 4 times for each 10°).

Therefore, the rate of evaporation at the given temperature after ozonization decreases almost 150 times.

In conclusion, several figures are given showing the absolute quantities of mercury evaporated from a 1 cm<sup>2</sup> area per second at 20°C, the rate of flow of air being 250 ml. for each 1 cm<sup>2</sup> of the mercury layer. From an unoxidized continuous surface -  $9 \cdot 10^{11}$ , from the surface of drops with a radius of 0.22 mm. -  $1.4 \cdot 10^{13}$ , from ozonized surfaces -  $6 \cdot 10^9$  atoms.

#### CONCLUSIONS

1. The relationship between the rate of evaporation of mercury droplets and their radii was studied under dynamic conditions at temperatures of 20 and 40°C.
2. The rate of evaporation from unit surface varies inversely with the radius of the drop.
3. A formula for calculation of the rate of evaporation of mercury droplets in a current of air is presented.
4. Upon oxidation of the drops by air, the diffusion of mercury vapor through the protective oxide film thus formed is greater, when the radius of the drops is smaller.
5. The rate of evaporation of the oxidized surface does not depend upon the radius of the drop.
6. The rate of evaporation and oxidation is many times greater in drops with a radius of several microns, than in drops with a radius of fractions of a millimeter.
7. After ozonization of the mercury surface, the rate of its evaporation decreases 150 - 200 times up to 40°C.
8. Upon raising the temperature still further, the protective nature of the oxide film is lost the quicker, the smaller the curvature of the surface.

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## TARTRATE COMPOUNDS OF TRIVALENT IRON

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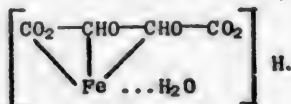
Tartrate compounds of trivalent iron have been repeatedly described in the literature, but the various authors do not agree as to the composition and structure.

Rosenthaler [1], in 1903 observed that  $\text{FeCl}_3$ , in the presence of tartrates, oxalates and citrates, does not give its characteristic actions with ammonium thiocyanate, with potassium ferrocyanide, with mixtures of starch and zinc iodide and with guaiacol. In 1908 Rosenthaler and Siebeck [2] obtained a basic iron tartrate with the formula  $2\text{Fe}_2(\text{C}_4\text{H}_4\text{O}_6) + 3\text{Fe}(\text{OH})_3 \cdot 3\text{H}_2\text{O}$ , by dissolving 20 grams of neutral  $\text{K}_2\text{C}_4\text{H}_4\text{O}_6$  in 180 grams of water and adding it to an excess of a boiling solution of 5%  $\text{Fe}(\text{NO}_3)_3$ ; after washing and drying they obtained a brownish yellow, amorphous, hygroscopic powder, easily soluble in water and insoluble in alcohol. This precipitate is also soluble in caustic alkalis and ammonia with the separation of the hydroxide. Cowley [3], working with iron citrate, also obtained the tartrate complex of trivalent iron by heating 4 gram-atoms of iron with 3 mols. of tartaric acid in a water bath; 4 equivalents of alkali were used up in the neutralization of the solution obtained. Paira [4] obtained a ferrotartrate complex in the form of a yellow, difficultly soluble precipitate by mixing 1 mol. of  $\text{FeCl}_3$  with one mol. of sodium tartrate and  $\frac{1}{2}$  mol. of  $\text{Na}_2\text{CO}_3$ . An evolution of  $\text{CO}_2$  takes place at this point. Following the addition of the  $\frac{1}{2}$  mol. of  $\text{Na}_2\text{CO}_3$  the precipitate dissolves with the further evolution of  $\text{CO}_2$ . The same precipitate forms with 2 mols of tartrate, but it is easily soluble upon warming. The analysis of the dried precipitate gives in %: Fe - 27.56, C - 23.68. The calculated % for the formula  $(\text{C}_4\text{H}_2\text{O}_6\text{Fe})\text{H}$  is: Fe - 27.58 and C - 23.63. The ferrotartronic acid is also easily formed from  $\text{C}_4\text{H}_4\text{O}_6$  and  $\text{Fe}(\text{OH})_3$  and separates upon warming. Ammonia does not precipitate  $\text{Fe}(\text{OH})_3$  from this solution and caustic alkalis form a precipitate only after prolonged boiling. Alkali salts of ferrotartronic acid are easily soluble in water, insoluble in alcohol, and may be recrystallized from dilute alcohol. Analysis of the sodium salt yielded in %: Fe - 17.81, Na - 7.54, C - 15.16, the calculated % for the salt  $(\text{C}_4\text{H}_2\text{O}_6\text{Fe})\text{Na} \cdot 5\text{H}_2\text{O}$  being: Fe - 17.78, Na - 7.30, C - 15.24. At 100-105°C it loses 20.11% water, which corresponds to 3.5 mols. At a still higher temperature, decomposition takes place with the formation of a ferro-salt. The potassium salt, dried at 100-105°C has the formula:

$(\text{C}_4\text{H}_3\text{O}_6\text{Fe})\text{K} + \frac{1}{2}\text{H}_2\text{O}$ . Found by analysis in %: Fe - 22.39; K - 15.62; C - 19.06. Calculated in %: Fe - 22.40; K - 15.60; C - 19.20.

In 1923, Simon [5] investigated the influence of  $\text{CuCl}_2$ ,  $\text{ZnCl}_2$  and  $\text{FeCl}_3$  on tartaric acid and found that different quantities of alkali were necessary for neutralization of the mixture. For iron,  $3\text{C}_4\text{H}_4\text{O}_6 + 3\text{FeCl}_3 + 11\text{KOH} = (\text{C}_4\text{H}_4\text{O}_6\text{K})_3\text{Fe} \cdot \text{Fe}_2(\text{OH})_5\text{Cl} + 8\text{KCl} + 6\text{H}_2\text{O}$  and further:  $(\text{C}_4\text{H}_4\text{O}_6\text{K})_3\text{Fe} \cdot \text{Fe}_2(\text{OH})_5\text{Cl} + \text{KOH} = (\text{C}_4\text{H}_4\text{O}_6\text{K})_3\text{Fe} \cdot 2\text{Fe}(\text{OH})_3 + \text{KCl}$ . In 1931, Smythe [6] titrated organic acids in the presence of copper salts and trivalent iron with a glass electrode and observed an increased acidity after mixing the acids with the salts. Upon titrating malic, tartaric and citric acids, ferric hydroxide does not separate and ammonia does not precipitate

it, which fact, according to the author, cannot be explained by the formation of colloidal solutions. Franke [7], in the same year found that yellow solutions form by the action of  $C_4H_6O_6$  or the tartrates of alkali metals, changing to green with excess of tartrate. . . An acid separates in the reaction. The solutions were investigated colorimetrically and also their pH determined. From a solution containing equimolecular quantities of tartrate and iron salt, a precipitate separates, which after analysis is shown to be ferrotartaric acid, discovered in 1914, by Paira,



The complex easily undergoes autoreduction by heating the dried material at 100°C or under the influence of light, this being evidenced by the change in color. The author also discovered complexes with the following formulas:  $\text{FeT}_3\text{Na}_6$  and  $\text{Fe}_3^{\text{II}}[\text{Fe}^{\text{III}}\text{T}_3]_2$  or  $\text{KFe}[\text{Fe}^{\text{III}}\text{T}_3]$ , where T stands for the tartrate radical. Pariselle [8] in 1931 and later [9] investigated the reversibility of solutions of  $\text{Fe}(\text{NO}_3)_3$  and  $C_4H_6O_6$  and established the maximum in equimolecular mixtures. Upon neutralization, a precipitate separates containing an atom of Na in the molecule. The following complex salts were found:  $\text{Fe}(C_4H_4O_6Na)_3$  and  $(C_4H_3O_6Na_2)_3\text{Fe}$ .

Not one of the formulas given in the literature for the ferrotartrate complex can explain the observation of Cowley, confirmed by us, of the ratio of 4 atoms of iron to 3 molecules of tartrate, nor the fact which we established that three equivalents of acid form for each atom of iron. It must be noted that at different temperatures and concentrations, as well as different ratios of the components, compounds are obtained with different formulas. Evidently, none of the authors worked with dilute solutions of iron salts and tartrates. Therefore, a separation of the complex and its analysis was undertaken.

#### EXPERIMENTAL

**Separation of the complex.** In view of the insolubility of the complex in alcohol, it is separated from solution in the cold by the addition of alcohol. To 300 ml. of a 10% solution of  $\text{FeCl}_3$  was added 33 grams of neutral potassium tartrate. The solution was chilled in order to avoid the hydrolysis of the complex. Then 5-7 drops of phenolphthalein were added and the solution neutralized with 2 N KOH to a rose color. The volume of the entire mixture was equal to 550 ml. At this point, 600 ml. of alcohol was added in order to have the final solution contain 50% alcohol. Here, a yellow precipitate of the complex separated out, contaminated with potassium chloride. The tartrate salt and the alkali used above was for the purpose of providing the same alkali metal, which would simplify further analysis. The precipitate obtained was dried on a watch glass at a temperature of 50-60°C in a drying oven. Not only can the precipitate not be dried on the filter paper, but it cannot remain there for any length of time, since the precipitate firmly adheres to the paper. Also, upon slow drying, the complex browns at the surface. The drying was continued to constant weight.

**Analysis of the precipitate.** The analysis was carried out in the following fashion. A definite weight of sample was ignited to constant weight and the loss on ignition calculated, which made it possible to determine the amount of tartaric acid in the complex. The residue from the ignition is washed on a filter paper 5 times with hot water. The washings are then cooled and quantitatively transferred to a 50 or 100 ml. volumetric flask, depending on the volume of the solution, and water added to the solution up to the mark. The  $\text{Fe}_2\text{O}_3$  remaining on the filter paper is washed still further until the disappearance of the  $\text{Cl}^-$  reaction, ignited and weighed. From the volumetric flask 20 and 30 ml. aliquots are pipetted out and the  $\text{K}_2\text{CO}_3$  formed in the ignition titrated in the presence of methyl orange to determine the amount of potassium. It is possible that a partial decomposition of the carbonate takes place

upon ignition. This increases somewhat the loss upon ignition, but the amount of alkali determined is not affected.

For the determination of the amount of KCl in the complex, the amount of Cl was determined individually, by gravimetric means in the originally-obtained complex, and volumetrically, by the Mohr method, in the wash water after the ignition. The results of the KCl determinations are given in Table 1.

Table 1

Experiment No.	Wt. of sample, g.	Found		Percent		Remarks
		AgCl(grams)	KCl (grams)	KCl in the complex	complex	
1	0.6239	0.3861	0.2011	32.20	67.80	Gravimetrically Volumetrically
2	0.5684	0.3523	0.1835	32.28	67.72	
3	0.4360	18.36 ml. 0.1 N AgNO <sub>3</sub> used in the titration	0.1396	32.03	67.97	

The percent of iron, potassium, and the loss upon ignition (Tables 2 and 3) were calculated on the basis of the pure complex, the content of which averaged 67.83% in the samples taken (Table 1).

The formula for the complex was determined by the percent composition. The number of molecules of tartaric acid present in the molecule of the complex was established by ignition, in the following fashion. Each mol. of the tartrate, upon ignition loses part of the carbon and oxygen and all of the water, forming K<sub>2</sub>CO<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>. Assuming that the iron is trivalent and takes the place of hydrogen in two of the hydroxyl groups, it must be admitted that the third valence takes the place of an entire hydroxyl group. Then C<sub>4</sub>H<sub>2</sub>O<sub>6</sub>K<sub>2</sub> loses 3C+2H+2O (three atoms of oxygen form the carbonate and one atom of oxygen remains combined with the iron). Also, a molecule of water separates from the two hydroxyl groups combined with the iron in different tartrate molecules. Thus, for each tartrate molecule the following loss occurs upon ignition: 3C+2H+2O+½H<sub>2</sub>O = 79.

TABLE 2

Experiment No.	Sample weight (grams)	Its complex content (grams)	Loss upon ignition (%)	Fe (%)
1	1.1377	0.7697	23.40	23.34
2	1.0462	0.7096	23.61	23.23
3	1.0280	0.6973	23.92	23.14
4	1.4218	0.9644	23.76	23.10
5	1.2803	0.7984	23.72	23.00
6	1.3006	0.8822	23.80	23.28
			23.71	23.18

We find the relative quantities of Fe and K atoms and of the molecules of tartaric acid in the complex to be - tartaric acid:Fe:K = 0.30:0.41:0.62 ≈ 3:4:6 i.e. three molecules of tartaric acid require 4 atoms of iron and 6 atoms of potassium, and the formula for the iron complex coincides with the formula for the aluminum complex, previously described by the author [10]:

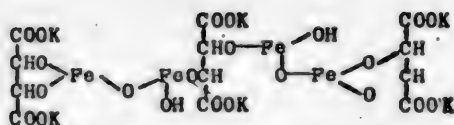


Table 3

Experiment No.	Sample weight (grams)	Its complex content (grams)	Volume of wash water	Volume taken for titration (ml)	Amount of 0.1 N HCl used (Average of two determinations) (ml)	K (%)
1	1.1377	0.7697	50	20	19.23	24.37
2	1.0462	0.7096	50	20	17.74	24.27
3	1.4218	0.9644	50	20	24.12	24.38
4	1.2803	0.7984	50	20	19.94	24.35

This formula agrees with that of Cowley and is confirmed by the author's ratio: 4 atoms of iron for 3 molecules of tartaric acid, and explains the separation of 3 equivalents of acid for each atom of iron, which was established by the author. Besides the potassium salt, a complex sodium salt was also precipitated and analyzed. The conditions for the precipitation are the same. The sodium salt is more viscous than the potassium. The precipitate easily adheres to the stirring rod, and is wound around it and removed. Water is more difficult to remove; the drying being carried out at 120°C.

Table 4

Experiment No.	Sample weight (grams)	AgCl found (grams)	Quantity of NaCl (grams)	Percent in the complex	Percent of complex
1	0.7845	0.7737	0.3136	39.97	60.03
2	0.4356	0.4305	0.1743	40.01	59.99
3	0.4884	0.4849	0.1963	40.19	59.81
					Average 59.94

The analysis was carried out in the same manner. The results of the analysis are shown in Tables 4, 5 and 6.

The ratios from the results found are: tartaric acid:Fe:Na = 26.34/79 : 25.85/56 : 15.95/23 or  $C_4H_6O_6:Fe:Na = 0.333 : 0.461 : 0.683 = 1 : 1.37 : 2.08 \approx 3 : 4 : 6$ , i.e., the composition of the sodium salt is no different from that of the potassium salt and it can be given given an analogous formula:

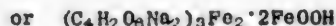
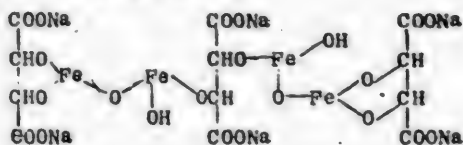




Table 5

Experiment No.	Weight of sample (g.)	Its complex content (g.)	Loss upon ignition (%)	FE (%)
1	1.2630	0.7570	26.19	25.80
2	1.4740	0.8835	26.39	25.92
3	1.4264	0.8540	26.42	25.95
4	1.6525	0.9915	26.30	25.84
5	1.5836	0.9492	26.38	25.76
Average			26.34	25.85

Table 6

Experiment No.	Weight of sample (g.)	Its complex content (g.)	Volume of wash water (ml)	Volume taken for titration (ml.)	Amount of 0.1 N HCl used (ml.)	Na (%)
1	1.2630	0.7570	50	20	21.28 } 21.30	15.91
				20	21.33 }	
2	1.4740	0.8835	50	20	24.40 } 24.44	15.90
				20	24.47 }	
3	1.4264	0.8540	50	20	23.75 } 23.74	15.98
				20	23.72 }	
4	1.6525	0.9915	50	20	27.63 } 27.61	16.02
				20	27.60 }	
5	1.5836	0.9492	50	20	26.20 } 26.26	15.95
				20	26.33 }	
Average						15.95

But in the literature, besides the salts of internal-complex metal tartrate acids, free acids were also described. Thus, Paira in 1914 obtained ferrotartaric acid of the following composition:  $(C_4H_2O_4Fe)H$ . The author had already separated and investigated aluminum tartaric acid. In order to confirm the existence of ferrotartaric acid and to determine whether under our conditions Paira's acid or an acid of another composition is formed, the precipitation with alcohol was repeated but without the preliminary neutralization. A yellow, flocculent, slimy precipitate settled out. After filtering through filter paper, the precipitate was removed from the paper and dried on a watch glass. The precipitate can not be dried on the filter paper because it adheres so strongly to it. The drying was first carried out in air and then in a drying oven at 105-110°C. The drying in air proceeded slowly, since the precipitate deliquesced. This can be explained by hygroscopicity or hysteresis. The dried precipitate had a brownish-yellow color with a greenish cast. It easily dissolved in water, alkalis and acids. The aqueous solutions had a definite acid reaction. An analysis was carried out on the precipitate, but besides the previous determinations, a determination of the amount of free carboxylic groups was also carried out. The results of the analysis are given in Tables 7, 8 and 9.

The analytical data permits the development of a formula. As in the previous experiment, the number of molecules of tartaric acid is found by the loss on ignition, but since there is no alkali metal in this complex and the carboxylic groups completely volatilize during ignition, the conditional molecular weight of tartaric acid will be different. This molecular weight was found by the following considerations. In the molecule of the complex there are 4 atoms of iron

Table 7

Experiment No.	Weight of sample (g)	Volume of 0.1 N AgNO <sub>3</sub> used (ml)	Amount of KCl (g)	Percent KCl	Percent of complex
1	0.4617	24.64	0.1836	39.76	60.24
2	0.5177	28.15	0.2090	39.86	60.14
3	0.4312	21.19	0.1578	39.70	60.30
Average				39.77	60.23

Table 8

Experiment No.	Weight of sample (g)	Its complex content (g.)	Loss upon ignition (%)	Fe (%)
1	1.2572	0.7572	56.45	30.45
2	1.4816	0.8924	56.48	30.60
3	1.5020	0.9047	56.38	30.54
4	1.4684	0.8844	56.36	30.56
5	1.6008	0.9642	56.42	30.58
Average			56.42	30.55

Table 9

Experiment No.	Weight of sample (g)	Its complex content (g)	Volume of 0.1 N NaOH used (g)	Carboxylic groups found in a molecule of the complex		
				Trisubstituted	Monosubstituted	Unsubstituted
1	0.6822	0.4114	32.51	6.7	6.1	5.8
2	0.4215	0.2540	19.39	6.5	5.9	5.6
3	0.5738	0.3400	27.10	6.5	6.0	5.75
Calculated:				3	5	6

for each 3 molecules of tartaric acid. Evidently only two or even one of the valences of the iron atom is substituted for hydrogen in the hydroxyl groups and its remaining valences combined with the hydroxyl groups. Upon ignition  $2\text{Fe}_2\text{O}_3$  remains, i.e. each mol. of tartaric acid yields the iron, and upon ignition, each molecule of tartaric acid loses  $4\text{C}$ ,  $6\text{H}$ ,  $4\text{O}$  and  $\text{OH}$ , which is:  $48 + 6 + 64 + 17 = 135$ . We assume that the conditional molecular weight of tartaric acid is 135. From this we obtain:

$$30.55/56 : 56.42/135 = 0.54 : 0.41 = 1.31 : 1 = 3.93 : 3 \approx 4 : 3.$$

i.e. also here, 3 mols. of tartaric acid require 4 atoms of iron. From Table 9 it is evident that if it is assumed that the molecule of the complex has three free carboxylic groups and the remaining three are substituted by potassium, then the amount of free carboxylic groups calculated from the titration data and from the corresponding molecular weight is 6.5,



although there should only be three. The supposition that there is one substituted carboxylic group and 5 free groups is also unconfirmed, and only for the unsubstituted complex, having 6 carboxyls does the calculation give 5.8 - 5.75, i.e. in rounded figures, 6 carboxyls.

It is of interest to compare the composition found for the sodium salts of the complex with the composition of compounds obtained by other authors (Table 10).

Table 10

Formula	Loss upon ignition (%)	% Fe	% Na	Author
$2\text{Fe}_2(\text{C}_4\text{H}_4\text{O}_6)_2 + 3\text{Fe}(\text{OH})_3$ . . . . .	60.92	27.35	--	Rosenthaler - Siebeck
$(\text{C}_4\text{H}_2\text{O}_6\text{Fe})\text{Na}$ . . . . .	40.88	24.88	10.22	Paira
$(\text{C}_4\text{H}_4\text{O}_6\text{Na}_3)_3\text{Fe} \cdot 2\text{Fe}(\text{OH})_3$ . . . . .	49.04	20.14	8.88	Simon
$\text{T}_3\text{FeNa}_3$ . . . . .	37.61	8.77	21.63	Franke
$\text{Fe}(\text{C}_4\text{H}_4\text{O}_6\text{Na})_3$ . . . . .	58.00	9.84	12.13	Pariselle
$\text{Fe}(\text{C}_4\text{H}_3\text{O}_6\text{Na}_2)_3$ . . . . .	37.32	8.88	21.73	Pariselle
$(\text{C}_4\text{H}_2\text{O}_6\text{Na}_2)_3\text{Fe}_2 \cdot 2\text{FeOOH}$ . . . . .	26.32	25.86	15.95	Pavlinova
Found by analysis . . . . .	26.34	25.85	15.95	

#### CONCLUSIONS

1. The separation of ferrotartaric acid, thus far not described in the literature, has been effected.
2. The formula of this acid was established, the presence of six carboxylic groups having been shown.
3. The identity of the formula for ferrotartaric acid with that of aluminum tartaric acid previously obtained was established.
4. The potassium and sodium salts of ferrotartaric acid have been separated and their formulas established by analysis.

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## POLAROGRAPHIC STUDY OF COMPLEX COMPOUNDS OF CADMIUM

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When Heyrovsky [1] introduced and developed the polarographic method of investigation, he indicated the possibility of applying it to the study of complex compounds. Lingane [2] developed this method and specified conditions necessary for obtaining accurate results. In spite of the great interest in the question of the application of polarography to the study of complex compounds, the amount of work done in this field is thus far quite small [2-6, 10, 17].

The dissociation constant of a complex which is reduced to the metal at the dropping mercury electrode can be found from the equation:

$$(E_H)_c - (E_H)_s = \frac{0.059}{n} \lg K_c - \frac{0.059}{n} \lg \frac{f_s k_c}{f_c k_s} - \frac{0.059}{n} p \lg C_x f_x \quad (1)$$

where  $K_c$  is - the dissociation constant of the complex ion;  $p$  - the fraction of the complexing agent entering into the complex ion (coordination number);  $(E_H)_c$  - the half wave potential of the complex ion;  $(E_H)_s$  - the half wave potential of the simple (uncombined in the complex) metal ion;  $k_c$  and  $k_s$  - the proportionality coefficients between the concentration and the diffusion current in Ilkovic's equation, for the complex and simple ions, respectively;  $f_c$ ,  $f_s$ , and  $f_x$  - the activity coefficients of complex ion, simple ion and the complexing agent;  $C_x$  - the concentration of the complexing agent;  $n$  - the valence of the metal or the number of electrons taking part in the reduction of the metallic ion.

However, in many cases the activity coefficients are unknown. Therefore, in many polarographic works a simplified equation is used. Thus for simplicity the following is assumed.

1)  $f_c = f_s$ . This supposition often closely answers to the activity in those cases where the valencies of the simple and complex ions are identical and the concentrations of the indifferent electrolyte in solutions of simple and complex ions are nearly equal. 2)  $f_x = 1$ . This simplification may lead to an actual error in the calculation, since with large concentrations of the complexing agent, its activity coefficient may differ greatly from 1, and also it may change in concentration. 3)  $k_c = k_s$ . This simplification very often exhibits a close correspondence to the activity, since the diffusion current constants depend, basically, upon the coefficient of diffusion (about one-half). The coefficient of diffusion of simple and complex ions usually only differ from each other by a negligible amount. After the introduction of these simplifications, equation (1) assumes a more simple form.

$$(E_H)_c - (E_H)_s = \frac{0.059}{n} \lg K_c - \frac{0.059}{n} p \lg C_x \quad (2)$$

The equation in this form was used for the majority of the investigations. In those cases where we had all the necessary data, we applied equation (1), in order to obtain, with its help,

a more exact value for  $K_c$ . In other cases we had to make several simplifications as indicated above.

The removal of the half-wave potential for any ion present in the solution by means of a complexing agent is rather frequently used in polarographic analyses to separate ions. Data on the polarographic nature of complex compounds is, however, quite fragmentary. (See, for example, the composite table collated from the literature up to 1941, or the half-wave potentials for inorganic substances in the monograph of Kolthoff and Lingane [6]).

In the present work we undertook the problem of the polarographic study of a series of complex compounds of cadmium, i.e. to study their compositions ( $p$ ) and the dissociation constant ( $K_c$ ). Cadmium, with its sharp polarographic wave, its moderately negative half-wave potential and its unique type of reduction at the dropping mercury electrode, is a convenient object of investigation. It forms a considerable number of different complex compounds with inorganic as well as organic complexing agents.

From another angle, the obtaining of systematic data on the different cadmium complexes in dilute solutions of cadmium should promote the development of the analytical chemistry of cadmium and, in particular, the development of new polarographic methods for its determination. Along this line, we concerned ourselves, in this work, with the examination of the criteria and limits of application of the polarographic method to the study of complex compounds (reversibility of the electrode process), and also with the accuracy of the data obtained by comparing our results with the data in the literature.

#### EXPERIMENTAL

The work was performed on a visual polarograph made by UFAN. To record the characteristic curves for each of the complex ions studies, photopolarograms were taken on an instrument constructed by Ukpriedmet. As an anode, a saturated calomel electrode was used, combined with the electrolyzer by the aid of an intermediate vessel with an agar-agar stopper, filled with a saturated solution of potassium chloride. All the potentials used in the present work are referred to the saturated calomel electrode.

Cadmium nitrate, prepared from the reaction of cadmium sulphate and carbonate, served as a source of cadmium. The concentration of the cadmium nitrate solution was determined analytically.

All the experiments were conducted at a temperature of 25°C (water thermostat). A series of experiments with the same complexing agent was carried out in the course of one day.

The value we found for  $E_{1/2}$  was used to correct for the d.c. resistance of the electrolyzer and a possible variance between the potential of the calomel electrode prepared in the laboratory and its theoretical potential. The first of these corrections is expressed by the drop in potential  $IR$  with a strong current flowing through the electrolyzer,  $I$  amperes and the resistance of the electrolyzer  $R$ . The second concerns itself with the difference between the theoretical and experimental values of the calomel electrode potential  $\Delta E$ . The sum of these corrections makes it possible to find the corrected ("theoretical") value of  $E_{1/2}$  from the experimentally found value of  $E_{1/2}$ .

$$(E_{1/2})_{\text{theoretical}} - (E_{1/2})_{\text{experimental}} = \frac{1}{2}IR + \Delta E. \quad (3)$$

The simplest method for finding the sum of the corrections is the comparison of the experimentally found value of  $E_{1/2}$  for any standard ion with its rigorously established value found from correction tables. For this purpose we used the thallium ion, whose half-wave potential in a 1 N solution of potassium nitrate was accurately measured by Lingane [6, p. 288] as 0.475 volts, relative to the saturated calomel electrode (Sat. C. E.). As is known, the choice of the thallium ion as a standard is due to the fact that the thallium ion has such a very slight tendency towards complex ion formation and therefore its half-wave potential depends very little upon the composition of the solution. Besides, the thallium wave is clearly defined, has the theoretical slope (reversible electrode process) and is situated in the region of small negative

potentials. Relative to the above, we have:

$$(E_{1/2})_{Tl\text{theoretical}} - (E_{1/2})_{Tl\text{experimental}} = \frac{1}{2} I_{Tl} R + \Delta E, \quad (4)$$

and

$$(E_{1/2})_{M\text{theoretical}} - (E_{1/2})_{M\text{experimental}} = \frac{1}{2} I_M R + \Delta E, \quad (5)$$

where M is - any ion (or particle in general) subjected to polarographic study.

If the concentration of the solution of thallium salt is so chosen that the diffusion current  $I_{Tl}$  is equal to  $I_M$  (in other words, so that the wave heights are equal), the right and left portions of equations (4) and (5) will be equal and the corrected value of  $E_{1/2}$  for the ion studied would be:

$$(E_{1/2})_{M\text{theoretical}} = (E_{1/2})_{M\text{experim.}} + (E_{1/2})_{Tl\text{theor.}} - (E_{1/2})_{Tl\text{experimental}}. \quad (6)$$

In those cases where the selected concentration of the thallium salt is for some reason or other unsuitable or undesirable, the corrected value for  $(E_{1/2})_M$  may be found in the following fashion. By determining  $E_{1/2}$  for any ion at two different concentrations (in our experiments we used the concentration ratio of 1:10), the d.c. resistance of the electrolyzer is found (more precisely, the system of - the actual electrolyzer - the intermediate vessel - the calomel electrode - the wires, combined with the polarographic system.)

As a result of this resistance, the values of  $E_{1/2}$  determined for a substance at different concentrations are somewhat different. For the two concentrations we have:

$$(E_{1/2})_{\text{theoretical}} = (E_{1/2})_{\text{experimental}}^I + \frac{1}{2} I^I R + \Delta E,$$

$$(E_{1/2})_{\text{theoretical}} = (E_{1/2})_{\text{experimental}}^{II} + \frac{1}{2} I^{II} R + \Delta E,$$

from which:

$$R = \frac{(E_{1/2})_{\text{experimental}}^{II} - (E_{1/2})_{\text{experimental}}^I}{\frac{1}{2} I^I - \frac{1}{2} I^{II}} \quad (7)$$

Substituting in (4) the found value for R and the experimentally determined  $I_{Tl}$  and  $(E_{1/2})_{Tl\text{exp.}}$  we obtain  $\Delta E$ , knowing which and with the help of equation (5) we obtain the corrected value of  $E_{1/2}$  for the ion studied.

$$(E_{1/2})_{M\text{theo.}} = (E_{1/2})_{M\text{exp.}} + (E_{1/2})_{Tl\text{theo.}} - (E_{1/2})_{Tl\text{exp.}} + \frac{1}{2} R (I_M - I_{Tl}). \quad (8)$$

In our experiments, all the corrections were as a rule quite small, not exceeding 0.01 - 0.02 volts, which indicated a normal potential for the saturated calomel electrode we used and a small d.c. potential drop in the electrolyzer. Calculations made from formula (7) gave 200 - 1000 ohms as the resistance of the electrolyzer.

#### Half-wave Potentials of Cadmium Complexes.

In order to obtain the polarographic characteristics of the complex compounds of cadmium, the half-wave potentials for cadmium complexes with various complexing agents were obtained.

A solution containing a considerable excess of the complexing agent was added to the solution of cadmium nitrate, gelatin added, and as an indifferent electrolyte, potassium nitrate was added (in experiments with ammonia and ammonium thiocyanate, ammonium nitrate was substituted). The total volume of the solution was adjusted to 25 ml. with water. The final concentrations of the components of the solution in these series of experiments were: cadmium -  $4 \cdot 10^{-3}$  M., the complexing agent - 1 M., potassium (ammonium) nitrate - 0.1 M., gelatine - 0.01%. The electrolyte is transferred from a volumetric flask to the electrolyzer, the dissolved oxygen



Table 1

## Shift in the half-wave potential of cadmium upon complex formation

Composition of the solutions:  $\text{Cd}(\text{NO}_3)_2 - 4 \cdot 10^{-3}$  M., complexing agent - 1 M., indifferent electrolyte - 0.1 M., gelatin - 0.01%. Definitions:  $m$  - mass of mercury flowing from the capillary (in mg. per sec.);  $\tau$  - the drop period of the capillary (in sec.);  $I$  - diffusion current ( $\mu\text{A}$ );  $I_D$  - diffusion current constant  $= I/m^2 \tau^{1/2}$ ;  $(E_{1/2})_c$  and  $(E_{1/2})_s$  the half-wave potentials of the complex and simple ions;  $\text{tg } \alpha$  - the tangential angle of inclination of the straight line expressed by the relation of  $E$  to  $\lg 1/I$ .

Complexing agent (concentration - molar)	Indifferent electrolyte (concentration 0.01 mols)	$m^2/\tau^{1/2}/s$ $\text{mg}^2/s \text{ sec}^{-1/2}$	$I$ $\mu\text{A}$	$I_D$	$\text{tg } \alpha$	$(E_{1/2})_c$ experimental V	$(E_{1/2})_c$ according to data in the literature	$(E_{1/2})_c - (E_{1/2})_s$
None . . . . .	$\text{KNO}_3$	1.67	25.2	3.8	0.038	-0.588	-0.586	0
Sodium citrate . . . . .	$\text{KNO}_3$	1.57	12.1	1.9	0.032	-0.71		-0.12
Citric acid . . . . .	$\text{KNO}_3$	1.23	12.8	1.6	0.036	-0.59		0
Sodium tartrate . . . . .	$\text{KNO}_3$	1.28	8.6	1.9	0.025	-0.70	-0.80	-0.11
Tartaric acid . . . . .	$\text{NH}_4\text{NO}_3$	1.27	13.5	2.6	0.035	-0.59		0
Ammonia . . . . .	$\text{NH}_4\text{NO}_3$	1.73	28.9	4.2	0.041	-0.797	-0.7	-0.209
Pyridine . . . . .	$\text{KNO}_3$	1.27	12.2	1.3	0.035	-0.65		-0.06
Aniline hydrochloride . . . . .	$\text{KNO}_3$	1.29	16.4	3.2	0.037	-0.64		-0.05
Potassium iodide . . . . .	none	1.83	27.9	3.9	0.041	-0.747	-0.74	-0.159
Sodium thiosulfate . . . . .	none	1.76	18.8	2.7	0.036	-0.73		-0.195
Ammonium thiocyanate . . . . .	$\text{NH}_4\text{NO}_3$	1.22	16.9	3.5	0.035	-0.66	-	-0.07
Cadmium cyanide . . . . .	$\text{KNO}_3$	1.28	14.2	2.8	0.032	-1.16	-1.18	-0.57
Perchloric acid . . . . .	none	1.30	15.5	3.0	0.0035	-0.62		-0.03

Fig. 1. Shift in  $E_{1/2}$  for cadmium upon complex formation.

Composition of the solutions:  $\text{Cd}(\text{NO}_3)_2 - 4 \cdot 10^{-3}$  M., complexing agent - 1 M.,  $\text{KNO}_3$ ,  $(\text{NH}_4\text{NO}_3) - 0.1$  M., gelatin - 0.01%. The half wave potentials for the cadmium complexes referred to the saturated calomel electrode is given at the left; at the right - the deviation of the half-wave potential for cadmium upon complex formation.  $E_{1/2}$  for  $\text{Cd}^{2+}$  is taken to equal -0.588 V (or 1 M.  $\text{KNO}_3$ ).  $(E_{1/2})_c$  for KCl was used on the basis of the data in the literature.

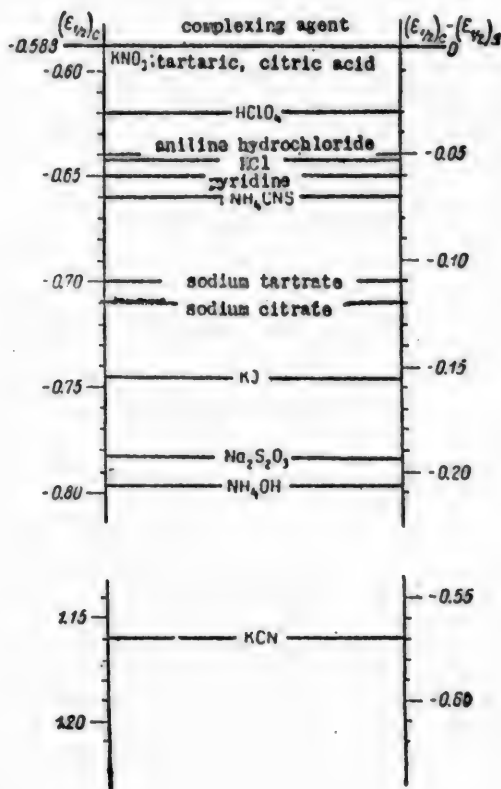
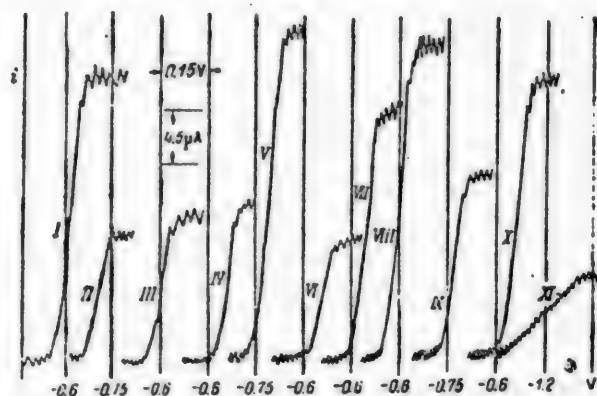


Fig. 2. Polarograms of various complexes of cadmium.



I - without a complexing agent; II - sodium citrate; III - citric acid; IV - sodium tartrate; V - ammonia; VI - pyridine; VII - aniline hydrochloride; VIII - Potassium iodide; IX - sodium thiosulfate; X - ammonium thiocyanate; XI - potassium cyanide. Composition of the solutions:  $\text{Cd}(\text{NO}_3)_2 - 4 \cdot 10^{-3}$  M.; complexing agent - 1 M.;  $\text{KNO}_3$ ,  $(\text{NH}_4\text{NO}_3) - 0.1$  M.; gelatin - 0.01%



removed by a stream of hydrogen for 20 minutes, and the solution run polarographically. The galvanometer scale readings were converted to microamperes, after deducting the readings for the corresponding residual current. On the basis of the experimentally obtained data graphs were constructed with the coordinates  $E$  and  $\lg 1/I-1$ , from which the half-wave potentials were determined [6].

The experimental results are shown in Table 1 and on Fig. 1, in which the complexing agents are placed in the order of increasing shift of  $E_{1/2}$  for cadmium. The polarograms obtained for different complexing agents are shown on Fig. 2.

From the data it is evident that the different complexing agents cause widely varying shifts in the half-wave potential of cadmium. By this shift, the stability of the complex may thus be judged and definite conclusions drawn for analytical purposes.

The cyanide complex of cadmium occupies a position sharply differentiated from the other complexes. A considerable shift in the half-wave potential attests to the great stability of the complex. The slight slope of the straight line expressing the relationship of  $E$  to  $\lg 1/I - 1$  (double the quantity of  $\lg \alpha$  in comparison with the  $\lg \alpha$  for the other investigated complexes), permits the assumption that here an irreversible reduction takes place at the mercury cathode.

The tartaric and citric complexes, which give a considerable shift in half-wave potential with their sodium salts, do not exhibit a marked shift if the corresponding acids are used as complexing agents.

Evidently, these complexes are stable only within certain limits of pH. This question is being studied.

Comparing the values we obtained for  $(E_{1/2})_c$  with the data given in the literature (Table 1), we notice that our results are similar to the results obtained by Kolthoff and Lingane (Cd without the complexing agent and in solutions of KI and KCN), and deviate somewhat from the data of the older works (Cd with ammonia and sodium tartrate). We do not know, accurately, the experimental conditions for ammonia and tartrates since these works were published in inaccessible journals, but from Kolthoff and Lingane's summary it is evident that the conditions of these experiments were different from ours. Thus, one of the authors (Dobryszewski) measured the reduction potential, tangentially drawn to the polarogram at an angle of  $45^\circ$ ; the other (Suchy) worked with Rochelle salt and not with sodium tartrate.

In the majority of solutions used in our experiments, we employed  $KNO_3$  as an indifferent electrolyte. From another standpoint, the half-wave potential for cadmium in a 1 M solution of  $KNO_3$ , in all these investigations, was taken as the standard potential (the half-wave potential of the simple, uncomplexed ion), in relation to which the shift of  $E_{1/2}$  upon complex formation was measured. It was therefore considered important to clarify the influence of the  $KNO_3$  added on the  $E_{1/2}$  of cadmium: this value, shown in Table 1, and which we used as a standard, was obtained in the following fashion. The half-wave potentials of cadmium and thallium in 1 M  $KNO_3$  were alternately determined, each time with a freshly prepared solution. From the average values, the corrected value of  $E_{1/2}$  for cadmium was calculated from equation (6).

Found:  $E_{1/2}$  of cadmium - 0.576; -0.560; -0.581; average -0.579;  $E_{1/2}$  of thallium: -0.464; -0.466; -0.468; average -0.466. Using the standard value of thallium in 1 M  $KNO_3$ , -0.475, we obtain the corrected value of  $E_{1/2}$  for cadmium -0.588 (Sat. C.E.). In the almost identical figure found by Kolthoff (-0.586) we see a confirmation of the accuracy of the methods we used.

We also determined the  $E_{1/2}$  of cadmium in solutions containing different concentrations of  $KNO_3$  (0.5 - 1.8 M). From Table 2, it can be seen that increasing the concentration of  $KNO_3$  practically does not change the half-wave potential of cadmium. Thus, a noticeable complex formation, which could shift the  $E_{1/2}$  does not take place here. This is also confirmed by Leden's [5] data which gives the value of 0.8 for the dissociation constant of the complex ion  $CdNO_3^+$ .

A small tendency (found at the limit of accurate measurement) toward an increase of  $E_{1/2}$  for cadmium with increasing  $KNO_3$  concentration may be explained by an increase in the ionic activity of the solution.

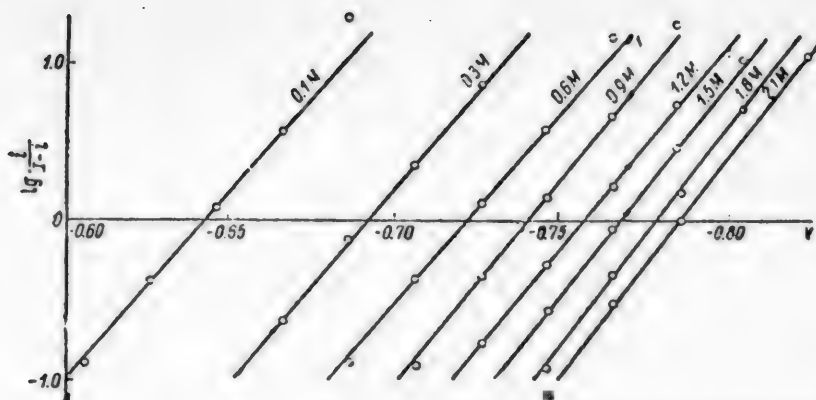


Fig. 3. Cadmium in solutions containing different concentrations of potassium iodide.

Composition of the solutions:  $\text{Cd}(\text{NO}_3)_2 - 4 \cdot 10^{-2} \text{ M.}$ ; gelatin - 0.01%; The concentration of KI, varying from 0.1 - 2.1 M., is indicated by the corresponding lines.

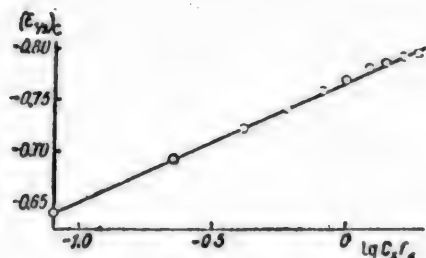


Fig. 4. Relation of the half-wave potential of cadmium in solutions of KI with the logarithm of the activity of KI

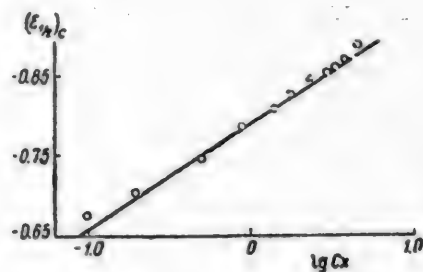


Fig. 5. Relationship of the half-wave potential of cadmium in solutions of  $\text{NH}_4\text{OH}$  to the logarithms of the concentration of  $\text{NH}_4\text{OH}$ .

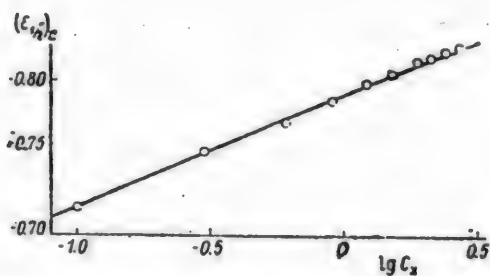


Fig. 6. Relationship of the half-wave potential of cadmium in solutions of  $\text{Na}_2\text{S}_2\text{O}_3$  to the logarithm of the concentrations of  $\text{Na}_2\text{S}_2\text{O}_3$

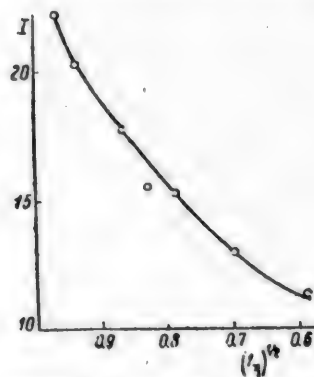


Fig. 7. Relation of the limiting current of the thiosulfate complex of cadmium to the viscosity of the electrolyte (by changing the concentration of  $\text{Na}_2\text{S}_2\text{O}_3$  in the solution).

This result agrees with Lingane's experiments [6]

We studied in greater detail the complexes of cadmium with potassium iodide, ammonia and sodium thiosulfate. We did not go further than these complexes because: 1) the considerable shift in the half-wave potential of cadmium simplified working with them; 2) these cadmium complexes are analytically important; 3) the proximity of the angular coefficient (see Table 1), 6th column,  $\text{tg } \alpha$ ) of these complexes to the theoretical value ( $\text{tg } \alpha = 0.030$ ) indicates a rather good reversibility of the electrode process [6]

Table 2

Half-wave potential of cadmium in solutions containing different concentrations of  $\text{KNO}_3$ .

Compositions of the solutions:  $\text{Cd}(\text{NO}_3)_2 - 4 \cdot 10^{-3} \text{ M}$ ;  $\text{KNO}_3 - 0.5-1.8 \text{ M}$ ; gelatin - 0.01%;  $m^{2/3} \tau^{1/6} = 1.82 \text{ mg.}^{2/3} \cdot \text{sec.}^{1/2}$ ;  $I_D = 3.5$ .

Molarity of the $\text{KNO}_3$	0.5	1.0	1.5	1.8
$E_{1/2}$ of cadmium . . . .	-0.584	-0.588	-0.589	-0.594

Cadmium in a solution of potassium iodide.

The preparation of the solutions for polarography was carried out as in the previous series of experiments. The potassium iodide used was the dried reagent grade. As a result of the considerable concentration of potassium iodide in the solution, an adequate electrical conductivity was assured and an indifferent electrolyte was not added to the solution. The final concentrations of the solutions were: cadmium nitrate -  $4 \cdot 10^{-3} \text{ M}$ ; gelatin - 0.01%; potassium iodide - from 0.1 to 3 M in 0.3 M. intervals.

On the basis of the experimental results, curves were drawn with the coordinates  $E$   $\lg i/i-1$  (Fig. 3) and with their help the values of  $E_{1/2}$  were found (Table 3). It is evident from the figure and the table that the limiting current remains constant upon increasing the concentration of the complexing agent. However, the half wave potential of cadmium shifts, regularly, to the more negative side.

Since  $p$  (the coordination number) is a small whole number, it is not necessary to have a greater degree of accuracy than that supplied by the original data, and we may assume  $K_C$ ,  $n$ ,  $k_C$ ,  $k_S$ ,  $f_C$  and  $f_S$  to be constants, thus transforming equation (1) to the form:

$$(E_{1/2})_C = a + b \lg C_X f_X$$

where  $b = \text{tg } \alpha = - \frac{0.059}{n} p$ . Having calculated, from the data in Table 2, a curve showing the relation of  $(E_{1/2})_C$  to  $\lg C_X f_X$ , and having obtained the slope of the resulting straight line, the magnitude of the complex portion of the ion is found.

In the cases we studied, (see Fig. 4)  $\text{tg } \alpha = 0.11$ ,  $n = 2$  and  $p = \frac{2 \cdot 0.11}{0.059} = 3.7 \approx 4$ .

It can be seen from the graph that in wide concentration limits, the cadmium potassium iodide is present in the solution in the form of the complex ion  $\text{CdI}_4^{2-}$ . Thus, on the basis of our experiments, we cannot confirm the data of Halder [7] on the existence of the complex ion  $\text{CdI}_3^-$ , obtained by the thermometric titration method. On the other hand, we cannot state anything concerning the iodine complexes of cadmium, containing smaller quantities of iodine, since according to Leden's work [8] they exist only in low concentrations of the complexing agent, while we worked with a large excess of the latter.

To calculate the dissociation constant of the cadmium iodide complex, we used equation (1) in its entirety. We will demonstrate our calculations with the following example.

Corresponding with equation (7), the resistance of the electrolyzer in our experiments

was shown to be equal to be equal to  $\frac{-0.760 - (-0.762)}{(13.6 - 1.4)10^{-6}} = 164$  ohms. The corrected value for  $(E_M)_C$  in 1 mol. of KI, according to equation (8), equals  $-0.742 + (-0.005) + \frac{164}{2} (27.9 - 21.7)10^{-6} = -0.747$  V. The shift  $(E_M)_C - (E_M)_S = -0.747 - (-0.588) = -0.159$  V.

Table 3

Shift in  $E_M$  for cadmium in solutions containing different concentrations of potassium iodide

$m^{2/3} t^{1/3} = 1.80 \text{ mg.}^{2/3} \cdot \text{sec.}^{-1/3}$  at  $-0.80$  V, average  $I = 27.9 \text{ } \mu\text{A}$ , average  $I_D = 3.9$ .

	Molarity of the potassium iodide solution.										
	0.1	0.3	0.6	0.9	1.2	1.5	1.8	2.1	2.4	2.7	3.0
I, $\mu\text{A}$ ...	26.5	28.5	28.4	27.9	27.9	27.1	29.1	28.7	28.1	28.6	26.5
$(E_M)_C$ , V...	-0.639	-0.689	-0.719	-0.737	-0.755	-0.765	-0.776	-0.783	-0.790	-0.794	-0.804

The ratio of  $k_C/k_S$  for equimolar concentrations of the complex and simple ions is equal to the ratio of the corresponding diffusion currents. In our example  $k_C/k_S = I_C/I_S = 27.9/25.2 = 1.11$ .

The ratio  $f_S/f_C$  for ions of equal valence and equal ion activity can be assumed to equal one (9), (since for the calculation of  $K_C$  we used the value of  $E_M$  for  $(\text{KI}) = (\text{KNO}_3) = 1$  mol.)  $f_x$  for 1 mol. of KI equals 0.68 (10). Substituting the data in formula (1), we obtain:

$0.03; \lg K_C = -0.159 + 0.03 \lg 1.11 + 0.03 \cdot 4 \lg 0.68 = -0.178$ .  
from which  $K_C = 1.2 \cdot 10^{-6}$ .

Calculation by the simplified formula (2) gives  $K_C = 5 \cdot 10^{-6}$ .

Leden [9], by the potentiometric titration method found  $K_C = 0.3 \cdot 10^{-6}$ . Other authors which he cited gave a somewhat higher value for  $K_C$  ( $0.4 \cdot 10^{-6} - 0.8 \cdot 10^{-6}$ ).

Thus, the results we obtained on the composition of the cadmium iodide complexes and their dissociation constants compare favorably with the results of potentiometric studies of these complexes.

#### Cadmium in ammoniacal solution.

The solutions for polarographic analysis were prepared as in the previous series of experiments. The ammonia used was freshly distilled. To avoid a considerable drop in the ammonia content of the electrolyte, the hydrogen, before being passed through the latter, was first passed through a trap filled with a solution of ammonia having the same concentration as the electrolyte. The capillary openings, through which hydrogen was passed through the trap and through the electrolyzer, and the depth of their immersion in the solutions were, as far as possible, of equal magnitude in both cases. Since the conditions were not completely identical in the trap and the electrolyzer, a drop in the ammonia concentration in the electrolyzer still took place. This drop reached 0.3 mole, with a concentration of 4-5 mols. of ammonia. It was determined for the various concentrations at which the experiments were conducted and taken into consideration in the calculations.

Because of the slight dissociation of ammonia, ammonium nitrate was added to the solution as an indifferent electrolyte, to raise the electroconductivity of the solution. The final concentrations of the solution were:  $\text{Cd}(\text{NO}_3)_2 - 4 \cdot 10^{-3}$  mols.,  $\text{NH}_4\text{OH}$  from 0.1 to 5 mols.,  $\text{NH}_4\text{NO}_3 - 0.1$  mols., gelatin - 0.01%.

The experimental results were analogous to those of the experiments with potassium iodide, and are shown in Table 4 and on Fig. 5. Not concerning ourselves with data on the activity of ammonia, we used the logarithm of the concentration as the abscissa in Fig. 5.



Table 4

Shift of  $E_{1/2}$  for cadmium in solutions of  $\text{NH}_4\text{OH}$  of different concentrations  
 $m^2/s \tau_{1/2} = -1.73 \text{ mg}^2/s - \text{sec.}^{-1/2}$  at  $-0.90\text{V}$ , average  $I = 28.9 \mu\text{A}$ , average  $I_D = 4.2$ .

	Molarity of the ammonia solutions										
	0.1	0.2	0.5	0.9	1.4	1.9	2.4	3.0	3.4	3.7	4.7
$I, \mu\text{A} \dots$ $(E_{1/2})_C, \text{V}$	29.9 -0.674	28.7 -0.700	27.7 -0.746	29.9 -0.783	29.5 -0.807	28.6 -0.824	29.4 -0.847	27.4 -0.851	28.6 -0.860	28.5 -0.870	29.4 -0.883

The tangent of the angle of inclination of the line shown on Fig. 5 equals 0.13. Therefore, there are four  $\text{NH}_3$  components in the complex of cadmium with ammonia.

However, the points found at the left portion of the curve show a tendency to form a line with a flatter slope, and the points to the right of the curve - a much greater slope, in comparison with the one shown. In this we see evidence that a series of cadmium complexes exists simultaneously in ammoniacal solutions. Their average composition for an  $\text{NH}_4\text{OH}$  concentration of 0.5 - 2 mols. is adequately expressed by the formula  $\text{Cd}(\text{NH}_3)_4^{2+}$ ; where at lower concentrations of  $\text{NH}_4\text{OH}$  we have a greater quantity of complexes poorer in ammonia, and at higher concentrations complexes richer in ammonia. This supposition is rather plausible, since for example, in ammoniacal solutions of copper, Bjerrum [15] established (potentiometrically) the simultaneous existence of several complexes of copper with ammonia, in which their relative composition varied with the concentration of ammonia.

The dissociation constant of ammoniacal cadmium complex was determined by the method described for the experiments with the iodide complexes, based on the following fundamental data:  $(E_{1/2})_C$  in 1 mol.  $\text{NH}_4\text{OH} = -0.797 \text{ V}$  (ref. Sat. C. E.);  $p = 4$ ;  $k_C/k_S = 1:1$ ;  $f_S/f_C$  - taken as unity from the considerations indicated above. Substituting the data in formula (1) we arrive at the value

$$K_C = 1.0 \cdot 10^{-7}.$$

The Chinese investigator Chi-Shou-Chu [11], studying the ammoniacal cadmium complexes polarographically, found  $p = 4$  and  $K_C = 3.3 \cdot 10^{-7}$ , which satisfactorily agrees with our data.

#### Cadmium in sodium thiosulfate solutions.

The solutions for polarographic study were prepared without using a supplementary indifferent electrolyte. The sodium thiosulfate was recrystallized. The final concentrations of the solutions used were:  $\text{Cd}(\text{NO}_3)_2 - 4 \cdot 10^{-3}$  mols.,  $\text{Na}_2\text{S}_2\text{O}_3$  - from 0.1 to 3.0 mols., gelatin - 0.01%.

The experimental results are given in Table 5 and on Fig. 6. Contrary to the experiments with potassium iodide and ammonia, where the diffusion current remained constant upon increasing the concentration of the complexing agent, in the present series of experiments the diffusion current dropped with an increase in the concentration of sodium thiosulfate. We assumed that this drop of the limiting current is connected with an increase in the internal friction in our polarographic solutions, since, as is known, solutions of  $\text{Na}_2\text{S}_2\text{O}_3$  possess a high viscosity. To verify this supposition, we carried out a series of viscosity measurements of solutions prepared for polarographic study, i.e. containing besides the complexing agent, cadmium nitrate, gelatin, and in the case of ammonia the indifferent electrolyte -  $\text{NH}_4\text{NO}_3$ , in concentrations indicated previously. The viscosity measurements were carried out at  $25^\circ\text{C}$  with the aid of a viscosimeter, through the capillary of which water flowed for about 30 seconds.

We found the following relative values for the viscosity ( $\eta$ ) of the solutions ( $\eta$  for water equals 1.00):

electrolyte without the complexing agent	-----	0.99,
electrolyte with 3 mols. of KI	-----	0.72
electrolyte with 5 mols. of $\text{NH}_4\text{OH}$	-----	1.10

Thus, in the case of solutions with ammonia and potassium iodide, the viscosity of the solution differs little from the viscosity of a solution with potassium nitrate.

The results of viscosity determinations for solutions of  $\text{Na}_2\text{S}_2\text{O}_3$ , where the value for  $\eta$  in a 3 M solution reaches 2.8, are shown in Table 5. Since there is quite a considerable increase in viscosity for solutions containing  $\text{Na}_2\text{S}_2\text{O}_3$ , a marked drop in the limiting current  $I$  may be expected in these solutions. In order to quantitatively verify this relationship, we constructed a graph expressing the relation of the limiting current  $I$  to the viscosity function  $(\frac{1}{\eta})^{1/2}$  (Fig. 7), based upon the following considerations. The viscosity coefficient  $\eta$  is inversely proportional to the diffusion coefficient according to the Stokes-Einstein equation:  $D = k_1 \frac{1}{\eta}$ . On the other hand, the diffusion coefficient enters into the well-known Ilkovic equation in the form  $I = k_2 D^{1/2}$ . From which,  $I = K(\frac{1}{\eta})^{1/2}$ . According to the proportionality between  $I$  and  $(\frac{1}{\eta})^{1/2}$ , we should have had a straight line on Fig. 7. The curvature of the graph which we obtained from our experimental data leads us to the conclusion that the drop in the diffusion current of cadmium with an increase in the concentration of  $\text{Na}_2\text{S}_2\text{O}_3$  cannot be explained simply by the increase in viscosity (in accordance with Ilkovic's equation).

Table 5

Shift in  $E_{1/2}$  for cadmium in solutions of sodium thiosulfate of different concentrations  
 $m^{2/3} \tau^{1/3} = 1.77 \text{ mg}^{2/3} \cdot \text{sec}^{-1/3}$  at  $-0.30 \text{ V}$ .

	Molarity of the Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> solutions										
	0.1	0.3	0.6	0.9	1.2	1.5	1.8	2.1	2.4	2.7	3.0
I, $\mu$ A	24.2	22.2	20.3	18.2	17.8	16.5	15.2	14.1	12.9	11.8	11.3
$\eta$	--	1.05	1.12	--	1.31	1.48	1.60	--	2.04	--	2.83
I <sub>D</sub>	3.4	3.1	2.9	2.6	2.5	2.3	2.1	2.0	1.8	1.7	1.6
(E <sub>1/2</sub> ) <sub>C.V</sub>	-0.700	-0.743	-0.765	-0.783	-0.796	-0.804	-0.814	-0.817	-0.822	-0.827	-0.842

Table 6

Composition and dissociation constant of the complex compounds of cadmium

Complexing agent	Author	Method	Formula of complex	Dissociation constant	Concentration of the complexing agent (moles/l)
Potassium iodide	measured by us Leden[8] *	Polarographic Potentiometric titration	$\text{CdI}_4^{2-}$	$1.2 \cdot 10^{-6}$	0.3-3.0
			$\text{CdI}_3^-$	$8.3 \cdot 10^{-3}$	
			$\text{CdI}_2$	$2.0 \cdot 10^{-3}$	0.01-0.4
			$\text{CdI}_3^-$	$1.0 \cdot 10^{-3}$	
			$\text{CdI}_4^{2-}$	$0.3 \cdot 10^{-6}$	
Ammonia	Halder **[7]	Thermometric titration	$\text{CdI}_4^{2-}$	---	0.5-2
			$\text{CdI}_3^-$	---	
			$\text{Cd}(\text{NH}_3)_4^{2+}$	$1.0 \cdot 10^{-7}$	
Sodium thiosulfate	measured by us	Polarographic	$\text{Cd}(\text{NH}_3)_4^{2+}$	$3.3 \cdot 10^{-7}$	0.1-3.0
			$\text{Cd}(\text{S}_2\text{O}_3)_3^{4-}$	$4.7 \cdot 10^{-7}$	

\* For convenience in the comparison, we recalculated Leden's figures, since the author used the inverse of the dissociation constant.

\*\* The dissociation constant in Halder's work was not determined.

The tangent of the angle of inclination of the line on Fig. 6 equals 0.09. Therefore, three complexes are present in the complex ion, i.e. the composition of the ion is  $\text{Cd}(\text{S}_2\text{O}_3)_3^{4-}$ . The points are well situated throughout the entire length of the line, which permits the supposition that the complex maintains a constant composition within wide limits of  $\text{Na}_2\text{S}_2\text{O}_3$  concentration.

Analogous to the above described method, the dissociation constant of the complex was calculated on the basis of the following data:  $(E_H)_C$  in 1 M.  $\text{Na}_2\text{S}_2\text{O}_3 = -0.783$  V,  $p = 3$ ,  $k_c/k_s = 4.5/6.5 = 0.7$  (the value of  $k_c$  is taken for 1 M.  $\text{Na}_2\text{S}_2\text{O}_3$ , since in the given case, I is not stable with an increase of  $C_x$ ),  $C_x = 1$  mol. (we could not find data on the activity of  $\text{Na}_2\text{S}_2\text{O}_3$ ). Considering the uniform decrease in the activity coefficient with increase in the valence of the ion, we took the ratio  $f_s/f_c$  equal to 2, based upon the comparison of the figures in the table given by Lewis and Randall [9, p. 267]:

then

$$K_c = 4.7 \cdot 10^{-7}.$$

We do not know of any data in the literature on the composition of the thiosulfate complexes of cadmium in aqueous solution or its dissociation constant. The older work of Euler [14] gives a value for a complex, whose composition in solution was not accurately established.

In Table 6 is shown a summary of the results we obtained in this work, and also, for comparison, different data found in the literature relating to the cadmium complex studied.

#### CONCLUSIONS

1. The polarographic half-wave potentials of cadmium in solutions of various complexing agents were measured.
2. By the polarographic method the coordination numbers and the dissociation constants of cadmium complexes with potassium iodide, ammonia and sodium thiosulfate were determined.

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# THEORY OF THE NITRATION OF SATURATED HYDROCARBONS AND THEIR DERIVATIVES.

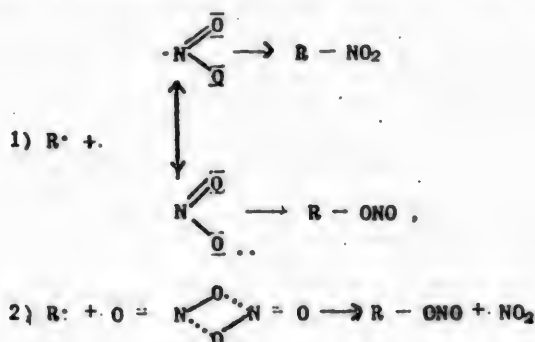
## VI. NITRATION IN THE SIDE CHAINS OF o- AND m-XYLOLS AND MESITYLENE.

A. I. Titov

As was shown in previous reports [1,2,3,4], the chemism of the nitration of paraffin chains by nitrogen oxides as well as nitric acid includes an initial reaction of the monomer form of nitrogen dioxide with a hydrocarbon:



and then a transformation of this radical with the formation of nitrocompounds, nitrites:



and nitrosocompounds



Depending upon conditions, the nitrites and nitrosocompounds may undergo quite a variety of transformations. The nitrites are chiefly transformed into the nitrates  $RONO_2$  and alcohols, which in their turn are converted into carbonyl compounds, acids and other products [4]. The basic transformation of the primary and secondary fatty-aromatic nitrosocompounds is their shift to the oxime and then to the hemi-dinitrocompounds. [2]:

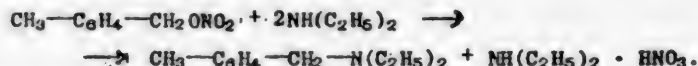


The formation of mononitrocompounds is favored by an increase in the concentration ratios  $NO_2/N_2O_4$  and  $NO_2/NO$ , which can be easily attained by raising the temperature to  $100^\circ C$ , resulting in the almost complete dissociation of the nitrogen dioxide dimer and in the removal from the liquid phase of the lower boiling oxides of nitrogen; the removal of  $NO$  is also effected by the introduction of oxygen into the sphere of reaction. On the basis of these conditions, more complete and detailed investigations were made on the nature of the synthesis of phenylnitromethane [3], and conditions were chosen for the nitration of m-xylyl to tolylnitromethane with a yield of 55% of theoretical. Nitrogen dioxide and nitric acid sp. gr. 1.5 were used with success as initial nitrating media in accordance with our theories and the application of the corresponding methods; the nitric acid served only as a source for the formation of nitrogen oxides and as a means for the transformation of nitrogen oxide to the dioxide.



For the synthesis of the tolyldinitromethanes  $\text{CH}_3-\text{C}_6\text{H}_4-\text{CH}(\text{NO}_2)_2$  corresponding to the mechanism of their formation from nitroso compounds, it was necessary to figure in, on the one hand, the increased degree of dissociation of  $\text{N}_2\text{O}_4$ , and on the other hand, the increased ratio of the concentration of nitrogen oxide to the concentration of nitrogen dioxide  $\text{NO}/\text{NO}_2$ . Practically, this was achieved by using a large excess of the hydrocarbon as a solvent-depolymerizer, first saturating the mixture with nitrogen oxide and conducting the reaction at room temperature in order to keep the nitrogen oxide in the sphere of reaction, concerning which more detailed material was shown previously [2]. An experiment, performed on the basis of these considerations, resulted in a yield for the m-tolyldinitromethane first obtained of 33.4% of the theoretical. It is extremely paradoxical that the formation of di-nitro derivatives and the suppression of the formation of mononitro derivatives in paraffin chains is caused by an increased dilution of the nitrifying agent and a lowering of the temperature, -- as is known, the direct opposite relationship is usually observed.

In the experiments with xylols, we did not investigate in detail the composition of the so-called residual oil - the remainder of the products of reaction after the extraction of the *o*-mono- and di-nitro compounds and toluic acids. To demonstrate the formation of m-xylol alcohol and its esters by the nitration of the paraffin chains of xylols, we limited ourselves to the determination of m-xylol nitrate by transforming it, by its reaction with diethylamine, into m-xyloldiethylamine.

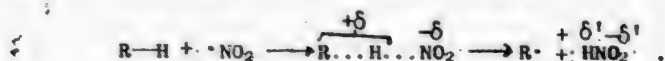


Without doubt, the composition of the residual oils in these experiments are completely analogous to the other cases we investigated [4, 5]. Depending upon the conditions of the reactions, the residual oil in these experiments contained at least xylol alcohol, its nitrite, nitrate and toluic acid ester, dixylol ether [5], toluyl aldehyde, toluic acid and ar-nitroxylols. Undoubtedly, detailed investigations would show the presence of a whole series of other different compounds - products of the transformation of nitrites, nitroso compounds - oximes and secondary products of the reaction of nitrogen dioxide in the benzene ring, which could also be very numerous, as was shown in our previous papers and in unpublished investigations. From such products, we were able to show, from our experiments with m-xylols, the formation of considerable quantities of hemi-tolyltrinitromethane and nitroxylenols.

The action of nitrogen dioxide on xylol and mesitylene was previously studied by Schaarschmidt [6]. Because of the evident imperfection of the method of investigation, the author was able to present only a few conclusions as to the composition of the products of the reaction. The author observed a sharp increase in the rate of reaction in the transition from toluol to m-xylol and mesitylene. The nitration of xylols and mesitylene to the mononitro derivatives by dilute nitric acid in sealed tubes under pressure was accomplished by M. I. Kononov [7].

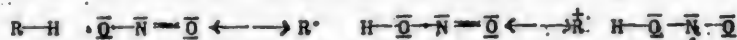
Of the general problems on the nitration of the side chains of methylbenzenes, we chose to examine the influence of methyl groups upon the speed of reaction. In accordance with the data of Kononov and Schaarschmidt, we observed that xylols are much easier to nitrate than toluols, and that mesitylene reacts very rapidly with nitrogen dioxide, even with warming.

As was explained before, the nitrogen dioxide radical-like monomer  $\text{NO}_2$  possesses a definite electrophilic nature, and from the point of view of Lewis' theory of acids and bases it can be related to aprotic acids of moderate strength; in short, the chemical nature of  $\text{NO}_2$  may be explained by the conception of an aprotic radical-acid. In the course of the reaction with hydrocarbons, the electrophilic and radical nature of nitrogen dioxide is effectively shown. This may be represented by the following diagram.

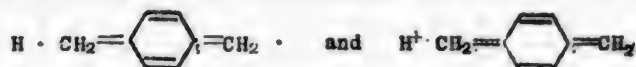


In the formation of the transitional complex, the nitrogen dioxide plays the role of an "acid", and the hydrocarbon the "base", i.e. the acceptor and donor of electrons, respectively; this process of releasing and coupling of electrons being considered as "neutralization".

On the basis of the above, and using the theory of resonance, the conclusions may be reached that the rate of reaction, determined by the observed rate of nitration, for the first step of the reaction of nitrogen dioxide with a hydrocarbon, will depend mainly on the degree of energy stabilization of the Radical  $R\cdot$  and the cation  $R^+$  structures in the transitional complex



The influence of aromatic nuclei upon the stabilization of structures of the type  $[ArCH_2]\cdot$  and  $[ArCH_2]^+$ , and consequently upon the rate of nitration of methylbenzene does not require special explanations. The positive action of methyl groups found in the ortho and para-positions to the  $NO_2$  methyl group attacked, may be understood if the possibility is considered of an added stability of the structures  $[CH_3C_6H_4CH_2]\cdot$  and  $[CH_3C_6H_4CH_2]^+$ , due to the introduction of  $\alpha$ -hydrogen into the resonance according to the formulation.



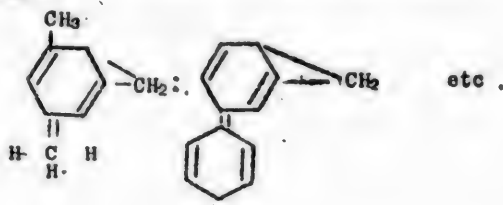
This conclusion is confirmed by a series of observations on the stabilization of o- and p-methyl radicals of the triarylmethyl type and their respective cations. Thus, for example, according to determinations by the method of Beyer [8], tri-p-tolylcarbinol is 2.5 times as strong a base as triphenylcarbinol; analogous data on the stabilization of p-methyl groups of triarylmethyls were obtained by measuring the degree of dissociation of hexaarylethanes.

The reason for the high degree of activity of the methyl groups in m-xylene and mesitylene is more difficult. Here, the attraction of the methyl groups by the usual inductive effect (+I) does not permit an explanation of the observed results, for example, the much greater chemical activity of mesitylene towards nitration in the side chains than o-xylene, since judging by the data on the nitration of toluene in the benzene ring [9], the activity of methyl groups in meta positions should be ten times weaker than for o- and p-methyl groups.

The considerable chemical activity of mesitylene in its action with  $NO_2$  in methyl groups may be better understood, if one bears in mind the stabilization of m-methyl radicals in the transitional complex followed by the formation of its free radical. The much greater stability of tri-m-tolylmethyl than triphenylmethyl and then the tri-p-methyl derivatives of the latter [10] may serve as an experimental basis for such a conclusion. In this connection, it may be also recalled that upon the introduction of phenyl groups into triaryl methyl, in the meta as well as the para positions, a similar sharp increase in the stability of the radicals is observed.

The ability of atoms and groups to increase the stability of free radicals and to increase the delocalization of the unpaired electron is called the exchange effect of these groups. It follows from the above that this effect varies in magnitude, depending upon the position in the benzene nucleus, except those positions where the Ingold effect appears.

The stabilizing influence of meta-substituents upon arylmethyls - their exchange effect, can be formally explained within the framework of the resonance theory, by the sharing, in the actual structure of the radicals, of a large number of possible structures with three-membered rings, for example:



## EXPERIMENTAL

### I. Nitration of *m*-Xylene

The hydrocarbon is separated from a technical mixture of xylenes by the method of Kishner and Vendelstein [11]. As concerns nitrogen dioxide, it exhibits a much greater activity than toluene, in conformity with the disruptive influence of the methyl group.

#### 1. Nitration of *m*-xylene by nitrogen dioxide to *m*-tolyl dinitromethane.

A mixture of 600 ml. of *m*-xylene, 20 grams of anhydrous copper sulfate and 10 ml. of nitrogen dioxide is allowed to stand at a temperature of 15-20°C in a flask, connected by ground glass to a tube of calcium chloride packed with calcium nitrate. Twice a day for the next 8 days, 10 ml. of nitrogen dioxide was added to the reaction mixture. In all, about 45 grams of nitrogen dioxide was used up in the reaction in this fashion.

25 days after the beginning of the reaction, the reaction mixture was treated according to the method developed for the synthesis of phenyldinitromethane from toluene [3]. After washing the hydrocarbon layer with water, it was agitated for three hours with 200 ml. of a 20% solution of potassium bicarbonate, adding in the second hour 30 ml. of a 50% solution of potash. The coarsely crystalline potassium salt of *m*-tolyl dinitromethane which separated out was drawn off by suction, washed with pure xylene, and then with alcohol and ether; 25.8 g. of the potassium salt were obtained. By the action of bromine on the bicarbonate extract remaining in solution, the dinitro product is converted into *m*-tolyl bromdinitromethane. 8.6 g. of the latter were separated; by treating it with alcoholic caustic it yielded 7.1 grams of the potassium derivative of *o*-hemi-dinitroxylene. The mother liquor from the bromination was acidified after adding bisulfite in order to separate *m*-toluic acid; 11.8 g. of the dried acid with a m.p. of 108-110°C was separated. The product obtained, when mixed with pure *m*-toluic acid, did not lower its melting point.

For the extraction of the mono-*o*-nitrosubstituted residue, it was agitated for 2 hours with 100 ml. of 20% potassium hydroxide, adding 5 ml. of diethylamine. On the next day, there separated from the alkaline extract 1.6 g. of a red, crystalline precipitate, probably the potassium salt of nitro-xylenol. Treatment of the solution with bromine gave 6.1 g. of a bromoderivative, which from calculations, we understood to be *m*-tolyl bromnitromethane  $\text{CH}_3\text{C}_6\text{H}_4\text{CBr}_2\text{NO}_2$ . After this the remainder of the reaction mixture was mixed with 30 ml. of diethylamine and heated 3 hours on a water bath. The reaction product was then treated with water and diluted with hydrochloric acid. The presence of considerable quantities of diethylammonium nitrate could be shown in the water extract, from which was also separated 0.3 g. of the potassium derivative of *m*-tolyl dinitromethane, formed from the corresponding *m*-hemitrinitro derivative upon reaction with diethylamine, concerning which more details will be given later. The acid extract of diethylamine, after the alkalization and evaporation on the water bath, was extracted with ether. From the ether layer, 3.8 g. of the amine was obtained, giving 6.9 g. of picrate. After recrystallization from alcohol, the picrate melted at 128-129°C and when mixed with the picrate of *m*-xylyldiethylamine, obtained from xylyl bromide (see further), did not produce a depression of the melting point. After evaporating the *m*-xylene under vacuum in a distilling flask, there remained 20.4 g. of the reaction product (residual oil). From this residue, by extracting with a 40% solution of bisulfite and agitating for three hours, 2.1 g. of *m*-tolyl aldehyde was separated, giving a semicarbazone with a m.p. of 216°C, which is in accordance with the data in the literature. The remaining residue of 17.9 g. was subjected to distillation under reduced pressure of 11 mm. and was evolved in the limits of 90-120°C, its composition not being investigated further. We will summarize the data obtained on the yields of the different derivatives and the degree of conversion for each of these in the reaction with *m*-xylene. For purposes of calculation, the residual oil is assumed to be nitroxylene.

m-Tolyltrinitromethane .....	0.3 g.	0.3 %
m-Tolyldinitromethane.....	27.7 g.	33.4%
m-Tolylnitromethane.....	4.0	6.2
m-Xylylnitrate.....	3.5	4.9
m-Tolyl aldehyde.....	2.1	4.1
m-Toluic acid.....	11.8	20.4
Residual oil.....	17.9	30.7

With a greater dilution of the hydrocarbon, a somewhat higher temperature (25-30°C) and a shorter time of standing, a higher yield of m-tolyldinitromethane could undoubtedly be obtained.

## 2. Nitration of m-xylene by nitrogen dioxide to m-tolylnitromethane

The reaction was conducted in the apparatus and by the method previously described for the synthesis of phenylnitromethane from toluene [3]. 36 g. of nitrogen dioxide and about 0.5 l. of oxygen were passed through a mixture of 200 ml. of m-xylene and 20 g. of anhydrous copper sulfate for three hours. As a result of treating with water, 150 ml. of 20%  $\text{KHCO}_3$ ; 150 ml. of 10%  $\text{NaOH}$  with the addition of 5 ml. of diethylamine, etc., as was previously described, the following yields were obtained, considered separately in grams and in the degree of conversion from the hydrocarbon.

m-Tolyltrinitromethane.....	0.4 g.	0.7%
m-Tolyldinitromethane.....	4.3 g.	6.9
m-Tolylnitromethane.....	26.4	54.7
m-Xylylnitrate.....	0.9	1.6
m-Tolyl aldehyde.....	2.1	4.1
m-Toluic acid.....	10.6	24.8
Residual oil.....	3.2	6.9

Contrary to phenylnitromethane, tolylnitromethane was obtained without decomposition by steam distillation (with the addition of 3 g. of urea) and almost without residue by distilling at 112-114°C at a reduced pressure of 10 mm.; by this method 22 g. of the pure derivative was obtained with  $n_D^{20}$  1.5300. If the reaction were carried out in the presence of excess oxygen and using a large quantity of m-xylene, much better results would undoubtedly be obtained.

## 3. Nitration of m-xylene to m-tolylnitromethane by nitric acid

Experiments were conducted to determine the maximum suitable conditions for the reaction [3] and the data given below should be examined in connection with the results obtained by the systematic investigation of the synthesis of phenylnitromethane from toluene; the method and procedures for the reaction were there described.

Into a mixture of 150 ml. of m-xylene, 10 ml. of nitric acid sp.gr. 1.4 and 1 g. of trioxymethylene, heated on a boiling water bath, 50 ml. of nitric acid sp.gr. 1.5 was gradually added in the course of 2 hours. After a half-hour's extraction, the reaction mixture was subjected to the usual treatment; determinations of the compositions of the residual oil were not carried out, except for m-tolyl aldehyde. The following yields of the separate derivatives were obtained:

m-Tolyldinitromethane.....	5.6 g.
m-Tolylnitromethane .....	29.1
m-Tolyl aldehyde.....	1.2
m-Toluic acid.....	12.8
Residual oil.....	3.7

The results obtained are very similar to the above-described data for the nitration experiment with nitrogen dioxide.



#### 4. Synthesis of *m*-xylyldiethylamine and its picrate

The *m*-xylyldiethylamine was prepared from *m*-xylylbromide by the method described for the synthesis of benzyldiethylamine. To ensure a product of high purity, it was dissolved in dilute hydrochloric acid, the insoluble mixture extracted with benzene, and then the amine was separated by alkali, dried with potash and distilled. After a double fractional distillation, a colorless fraction with a boiling point of 229°C (755 mm.) was collected. Investigation of the *m*-xylyldiethylamine gave the following results:

$d_4^{20}$  0.8966;  $n_D^{20}$  1.5002;  $MR_D$  58.08

Calculated  $MR_D$  57.95.

8.088 mg. substance: 0.591 ml.  $N_2$  (17°C, 734 mm)

Found %: N 8.31.

$C_{12}H_{16}N$ . Calculated %: N 7.91

The picrate of *m*-xylyldiethylamine was separated by mixing an alcoholic solution of the amine and picric acid. After recrystallization from alcohol, it formed bright yellow prismatic crystals with a m.p. of 128°C.

8.290 mg. substance: 1.068 ml.  $N_2$  (27°C, 732 mm.)

9.588 mg. substance: 1.225 ml.  $N_2$  (30°C, 729 mm.)

Found %: N 14.11; 13.75.

$C_{16}H_{22}O_7N_4$ . Calculated %: N 13.80

#### 5. Investigation of *m*-tolylidinitromethane

For the isolation of *m*-tolylidinitromethane, its potassium salt described in the experiment (I, 1), was used. After a single recrystallization from water, it was obtained in a very pure form. The free dinitroderivative was separated from a saturated aqueous salt solution or from a suspension acidified with hydrochloric acid to an acid reaction with Congo red. The colorless precipitate which formed was filtered and washed with water, dried in air and recrystallized from alcohol or petroleum ether.

The substance forms thick, colorless prisms with a m.p. of 54.5°C. Its structure, like *m*-tolylidinitromethane, is shown not only by its method of synthesis, but by the following data:

4.647 mg. substance: 0.561 ml.  $N_2$  (16°C, 752 mm.)

Found %: N 14.11.

$C_8H_8O_4N_2$ . Calculated %: N 14.27.

The substance is a monobasic acid; its potassium derivative  $m\text{-CH}_2\text{C}_6\text{H}_4\text{CK}(\text{NO}_2)_2$  is easily obtained by the action of potassium carbonate or bicarbonate and crystallizes well from hot water.

0.4054 g. substance: 0.1522 g.  $K_2SO_4$ .

Found %: K 16.86.

$C_8H_7O_4N_2K$ . Calculated %: K 16.71.

Upon heating in a test tube, the substance evolves nitrogen oxides, which is very characteristic for fatty-aromatic *o*-hemi-dinitrocompounds. Upon slowly raising the temperature in a capillary, the derivative begins to decompose at 125°C.

Like phenyldinitromethane, the substance is converted to *m*-toluic acid with a good yield, when heated for two hours at 100°C with 90% sulfuric acid. After recrystallization from hot water, the derivative melted at 111°C and did not depress the melting point when mixed with known *m*-toluic acid. This conversion also indicates that both nitrogroups are situated on the same hydrocarbon side chain.

The action of bromine upon solutions of alkali salts of *m*-tolylidinitromethane immediately brings about a separation of oily drops corresponding to the bromoderivative. If alcoholic potassium hydroxide is added to the *m*-tolylidinitrobromomethane obtained, the potassium salt of *m*-tolylidinitromethane quickly separates; the latter separates in the free condition

upon the action of mixtures of solutions of iodides and sulfite salts with the bromoderivative.

## II. Nitration of o-xylene to o-tolyldinitromethane

The investigation of the nitration of o-xylene had a definite purpose - to obtain o-tolyldinitromethane, unknown up to the present time, and at the same time to show the general applicability of our method of obtaining  $\alpha$ -dinitroderivatives directly from the fattyaromatic hydrocarbons.

100 ml. of pure o-xylene was mixed with 5 ml. of nitrogen dioxide and 10 g. of anhydrous copper sulfate and allowed to stand at a temperature of 15-20°C. Twice a day for the next seven consecutive days, another 5 ml. of nitrogen dioxide was added to the reaction mixture. After 25 days, the product of the reaction was treated consecutively with water and with 200 ml. of a 10% solution of potassium bicarbonate.

The bicarbonate extract was evaporated on a water bath until crystallization started in the cold. The precipitated potassium salt of o-tolyldinitromethane was recrystallized from hot water, from which it separated in the form of long, needle-like, yellow crystals. From the solution of the salt obtained, free  $\omega$ -dinitro-o-xylene separated upon acidifying with dilute hydrochloric acid. At first it separated in the form of an oil, but it crystallized after cooling the mixture in ice and rubbing with a stirring rod. 5.1 g. of a fairly pure derivative was obtained. By treating the mother liquor, containing potassium salts, with bromine another 4.4 g. of tolyldinitromethane was separated as its  $\omega$ -brom derivative, which, upon treating with alcoholic caustic yielded more of the pure salt of o-tolyldinitromethane.

Upon recrystallization from petroleum ether, the substance precipitated in the form of thick prisms, colored a light yellow, with a m.p. of 42°C and with an initial decomposition point at 115°C. The method of synthesis, the results of the analysis and investigation of the chemical properties corresponded to a structure similar to o-tolyldinitromethane.

3.702 g. substance: 0.498 ml.  $N_2$  (16°C, 752 mm.)  
Found %: N 14.17  
 $C_9H_8O_4N_2$ . Calculated %: N 14.27

Upon heating it with 90% sulfuric acid and a small quantity of ammonium sulfate the substance was converted to o-toluic acid, melting at 103°C after recrystallization and not depressing the melting point when mixed with the known pure derivative. By treating a solution of the salt of the hemi-dinitroderivative with bromine, an oily bromoderivative separated, which congealed upon cooling. The potassium salt of o-tolyldinitromethane may again be obtained by the action of alcoholic potassium hydroxide upon the bromoderivative. Upon heating the  $\omega$ -dinitroderivative rapidly, nitrogen oxides are evolved. The bicarbonate extract, after the separation of o-tolyldinitromethane, yielded 10.3 g. of o-toluic acid upon acidification.

By treating the main reaction mixture, after the separation of  $\omega$ -dinitroxylene, with 50 ml. of 10% alkali mixed with 5 ml. of diethylamine, followed by the action of bromine, 2.6 g. of an oil was separated, which is probably o-tolynitrodibrommethane  $CH_3C_6H_4CBr_2NO_2$ . The residue from the reaction was heated for 3 hours on a boiling water bath with 10 ml. of diethylamine and as a result 1.1 g. of a base was separated from the mixture, probably o-xylyldiethylamine, which was not investigated further.

After distilling off the excess o-xylene in a vacuum at 20 mm., the residual oil amounting to 11.4 g. was fractionated:

I fraction . . . . .	60-85°C	2.7 grams
II fraction . . . . .	90-110	1.6
III fraction . . . . .	115-155	4.6
Residue . . . . .		2.0

From the first fraction the semicarbazone was obtained with a m.p. of 216-217°C corresponding with the data in the literature for the derivative of o-toluyaldehyde.

The use of a large excess of the hydrocarbon and a shorter standing period at a somewhat higher temperature (about 25°C) should lead to a considerable increase in the yield of o-tolyldinitromethane.

### III. Action of nitrogen dioxide with mesitylene.

At room temperature, nitrogen dioxide reacts very energetically with mesitylene. In this case, the reaction results chiefly in the formation of tarry products, possessing a weakly acid character and was not investigated closer. We will limit ourselves to the description of one of the preparatory experiments.

150 ml. of mesitylene was mixed at room temperature with 10 ml. of nitrogen dioxide. A marked temperature increase immediately took place. The next day the presence of nitrogen oxides in the reaction mixture could not be observed. Using the treatment described for the reaction with m-xylene, the formation could be shown in this reaction of about 0.6 g. of m,m-xylyl aldehyde, identified by semicarbazone, 1.1 g. of m,m-xylyldinitromethane, 1.6 g. of carboxylic acids and 1.5 g. of ar-nitromesitylene.

The m,m-xylyldinitromethane first separated was obtained in the form of the potassium salt by evaporating the potash extract. After recrystallization of the salt from water and acidifying it, a solution of free 1',1'-dinitromesitylene was obtained. Upon recrystallization from a water alcohol mixture, it formed thick, colorless prisms with a m.p. of 61-62°C and an initial decomposition point with liberation of gases at about 140°C.

3.994 mg. substance: 0.453 ml.  $N_2$  (17°C, 751 mm)  
Found %: N 13.58.  
 $C_9H_{10}O_4N_2$ . Calculated %: N 13.39.

An investigation of the action of nitric acid on mesitylene in a solution of acetic acid showed that the formation of nitro derivatives and oxidation of hydrocarbons in the paraffin chains took place only in the presence of nitrogen oxides. The same was shown for the reaction of durene with nitric acid sp. gr. 1.36.

### CONCLUSIONS

1. The mechanism for the activating action of methyl groups on reactions of side chains of polymethylbenzenes with monomer nitrogen dioxide was investigated. The conception of exchange effects of atoms and groups was introduced.
2. The reaction of nitrogen dioxide with m-xylene was investigated under conditions favorable to the formation of m-tolyldinitromethane and m-tolynitromethane. The formation of m-xylynitrate, m-toluyaldehyde and acid and m-tolyltrinitromethane, in these reactions, was experimentally shown.
3. A convenient method was given for the synthesis of m-tolynitromethane by the nitration of m-xylene with strong nitric acid.
4. A preliminary investigation of the reaction of nitrogen dioxide with o-xylene and mesitylene at room temperature was conducted, the formation of  $\alpha$ -hemi-dinitrocompounds, aldehydes and acids being shown.

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# MECHANISM OF THE CATALYTIC NITRATION OF AROMATIC COMPOUNDS IN THE PRESENCE OF MERCURY SALTS

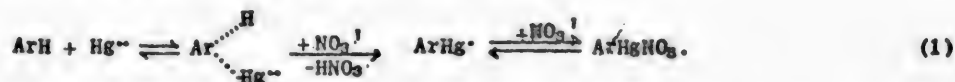
## II. GENERAL THEORY OF THE REACTION. REACTION OF MERCURO-AROMATIC COMPOUNDS WITH NITRIC ACID

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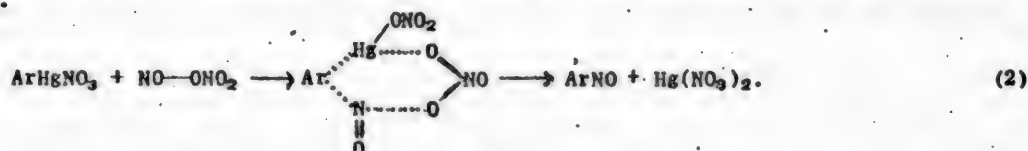
The K. E. Voroshilov Scientific-Research Institute of Organic Intermediates and Dyes

As follows from the general theory of nitration [1] developed by one of us, from the data of the first report [2], and from our work, "The Oxidative Nitration of Aromatic Nitroso-Compounds and Arylhydroxyamines" [4], the mechanism of catalytic oxidation and nitration by nitric acid in the presence of mercury salts consists of the following steps.

### I. Formation of a mixed mercurio-aromatic compound [3]:



### II. Conversion of the mercury compounds into nitroso compounds, as in the reaction with $\text{N}_2\text{O}_4$ :



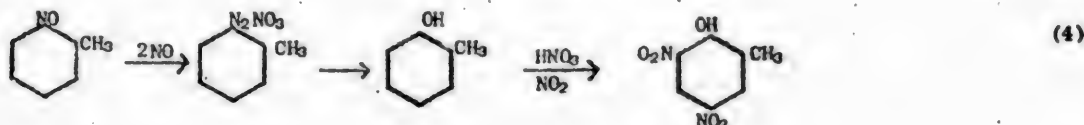
### III. Reaction of these nitroso compounds with nitric oxides and hydrogen ion, leading to the observed mixture of products produced by catalytic nitration.

The indicated reactions are still more complicated for nitroso compounds lacking a strongly electrophilic substitute such as the nitro group, and possessing a free para-position. For example, for o-nitrosotoluene they can be basically shown by the following reactions:

#### 1) Oxidation to a nitro compound:

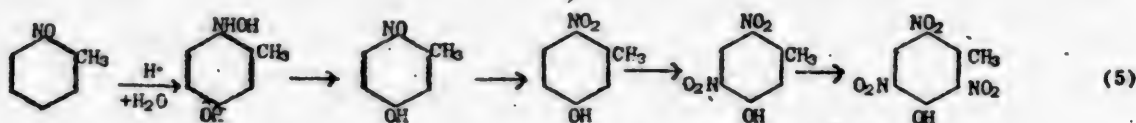


#### 2) Formation of diazo compounds and normal nitrophenols, whose hydroxyl is in the position previously substituted by the nitroso group:

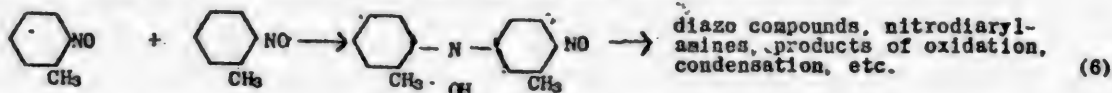




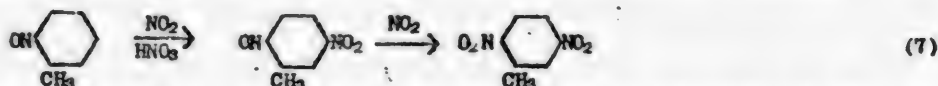
3) Conversion of ArNO under the action of hydrogen ion into a p-hydroxyarylhydroxylamine, and further oxidation and nitration of the latter into so-called anomalous nitrophenols, whose hydroxyl is in the para-position to that previously substituted by the nitroso group.



4) Condensation to p-nitrosodiarylhydroxylamines and further reaction of the latter:



5) Nitration in the para-position, and further transformation into dinitro compounds:



The relations between these five types of reaction of nitroso compounds are determined by the magnitudes of the concentrations of hydrogen ion, oxide, and dioxide of nitrogen. As a rule, the usual conditions of nitration in the presence of mercury salts result ultimately in the formation of a mixture of nitro compounds (equation 1) and anomalous nitrophenols (equation 3). However, as we shall show in later communications, it is possible under suitable conditions to realize the other types of reaction.

Nitroso compounds with nitro groups in their structure, such as m-nitronitrosobenzol, or any substitute in the para-position, such as p-nitrosotoluol, are more stable under the conditions of nitration, but can still react according to equations 1 and 2.

Of the steps of catalytic nitration we have indicated, the mercuration of aromatic compounds proceeds under usual conditions at the least velocity -- it limits the observed speed of the reaction. The transformation of mercurio compounds into nitroso compounds at suitable concentrations of nitrogen oxides usually takes place fairly rapidly; the reaction of the nitroso compounds also takes place rapidly. Because of this, the intermediate formation of an aryl mercury nitrate in the reaction of mercury salts with benzene and nitric acid can be observed only in the absence, or in the presence of very low concentration, of nitrogen dioxide in the reaction zone [3].

The above indicated results of our earlier work suffice for a rational explanation of all the results, including the most paradoxical, obtained earlier in the nitration of aromatic compounds in the presence of mercury salts. They have served to guide us in the discovery of new phenomena in this field.

But before turning to the discussion of these questions, we consider it necessary to supplement our earlier results [2] with new experimental data on the nitration of mercury compounds, indicating how their behavior under different conditions of reaction actually confirms the development of our theory. In addition, these data will offer more detailed confirmation of the intermediate formation of nitroso compounds in the nitration of mercury derivatives than was given in the introductory part of our preceding communication [4].

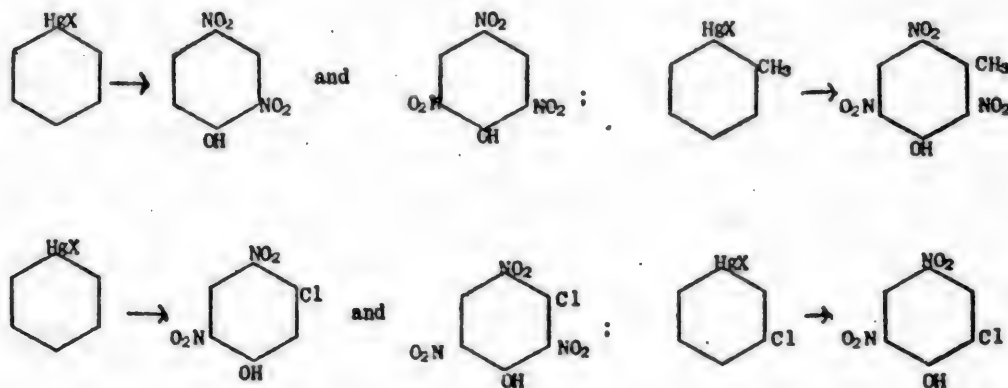
The initial formation of nitroso compounds during nitration of mercury derivatives was easiest to observe when they were relatively stable under experimental conditions. As followed from previously reported results, this requirement was best satisfied by nitroso compounds possessing a nitro group in any position, or another substitute in the para-position. In accordance with this, we succeeded in preparing nitroso compounds in fairly good yield

during the "nitration" with nitric acid in the presence of nitrogen oxides of the salts of *m*-nitrophenylmercury, *p*-tolylmercury, and *n*-chlorphenylmercury (experiments 1-4). Depending upon the conditions of the experiment, the indicated types of nitroso compounds which were formed were oxidized at this or another stage to the corresponding nitro compounds according to an equation of type (3) -- actual nitration in the proper sense of the word -- and also partly transformed into diazo salts, which in their turn could be converted into normal nitrophenols according to an equation of type (4). The characteristic peculiarity of the "nitration" of mercury compounds is that only the indicated types appear, and that there is an absence of the formation of anomalous nitrophenols according to an equation of type (5) and dark colored tarry products of polymerization of nitroso compounds according to equation (6).

Arylmercury compounds of all types were very uniformly transformed in dilute nitric acid (sp. g. 1.1-1.2) upon the latter's saturation with nitric oxide. Through the intermediate formation of nitroso compounds they were almost quantitatively changed by the action of nitric oxide into diazo salts according to equation (4), in a manner analogous to that found earlier in the experiments of Basberger and Mesemaynov [5] in a study of the reaction of mercury aromatic compounds with nitrous anhydride in organic solvents. Upon heating of the solvents, the diazo compounds are more or less easily transformed into nitrophenols, with the hydroxyl in the position earlier substituted by the mercury atom and then by the nitroso group. For example, *o*-chlorphenylmercuroacetate in this manner is converted into 4,6-dinitro-*o*-chlorphenol (experiments 5-8).

In the reaction of mercury compounds under analogous conditions, but at a higher temperature, and in the case of instability of the corresponding diazo compounds, only nitrophenols of the indicated types appear as observed products of the reaction; thus, in the nitration of *o*-tolylmercury with nitric acid, sp. g. 1.1 at 60°C, dinitro-*o*-cresol was obtained (experiment 8).

The most important results for an understanding of the mechanism of catalytic nitration in the presence of mercury salts were obtained from the reaction of concentrated nitric acid upon mercuroaromatic compounds with a free para-position, and in the absence from the molecules of highly electrophilic nitro groups. Corresponding to the theory, under suitable conditions, as close as possible to those of catalytic nitration, the intermediate formation from mercury compounds of such nitroso compounds took place fairly smoothly according to an equation of type (5), with an ultimate yield of up to 70% of theoretical of anomalous nitrophenol, possessing a hydroxyl para to the position earlier substituted by the mercury atom. In this manner reacted, for example, phenylmercuric acetate, diphenyl mercury, *o*-tolylmercuric acetate, di-*o*-tolyl mercury, *o*- and *m*-chlorphenylmercuric acetate (experiments 9-11).



The above-indicated reactions of mercurioaromatic compounds in all cases were accompanied by the formation of small quantities of the corresponding mononitro compounds, formed by the partial oxidation of the intermediate nitroso compounds according to equation (3). Under favorable conditions there could also be demonstrated the presence in the product of the reaction of small quantities of diazo compounds corresponding to the normal nitrophenols, and also p-dinitro compound (in the nitration of phenylmercuric acetate), formed from the nitroso compound according to equations (4) and (7). Because of its basic reaction -- the formation of anomalous nitrophenols -- this aspect of nitration may be called the oxidative nitration of mercurioaromatic compounds.

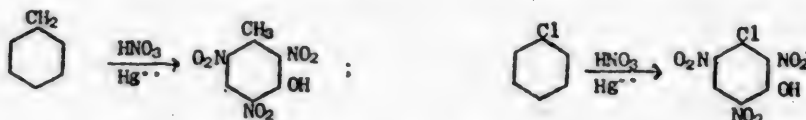
We must point out that the nitration under similar conditions of the mercury compounds of chlor- and brombenzol was studied by Hanke [c]. However, as a result of the imperfection of his method of investigation, he obtained in the reactions with o- and p-halophenylacetates only the corresponding nitrohalobenzenes. Upon nitration of m-brom and chlorphenylmercuric acetate he found no halonitrobenzenes in the product, but obtained materials with melting points of 118 and 110°C respectively, without determining their structures. In accordance with the results of experiment 10b, the reaction, under conditions given by Hanke, takes place in the manner we have indicated, accompanied, in the cases of nitration of o- and m-halophenylmercuric acetates with the predominant production of anomalous nitrohalophenols; in particular, the compounds obtained by Hanke appeared to be the respective 2,4-dinitro derivatives of ortho-bromophenol and orthochlorophenol.

The action of concentrated nitric acid upon mercury compounds with free para positions at low temperature is accompanied, especially in the nitration of phenylmercuric acetate, by a significant formation of dark colored and tarry products (experiment 12). Comparison of these results with the observed similar formation under analogous conditions of nitroso compounds and p-nitrosodiarylhydroxylamines gives a basis for considering that the formation of colored and tarry materials is due to the formation of intermediate nitroso compounds in accordance with equation (6).

Let us now consider the explanation of the results of investigation of catalytic nitration of various aromatic compounds in the presence of mercury salts.

In accordance with theory, the catalytic nitration of benzene with nitric acid, sp. g. about 1.35, gives 2,4-dinitrophenol, picric acid, nitrobenzene, and p-dinitrobenzene in proportions corresponding to those found in the nitration under analogous conditions of nitrobenzene (4) and phenylmercuric acetate (2).

On the basis of theories suggested previously, it was impossible to discover a satisfactory explanation of the path of formation of the most interesting products of the catalytic nitration of toluene (7) and chlorbenzene (8) -- trinitro-m-cresol and trinitro-m-chlorophenol, respectively.



From our point of view, these results are completely comprehensible. From the mercury compounds of toluene (1,2) and chlorbenzene (3,4) first formed:

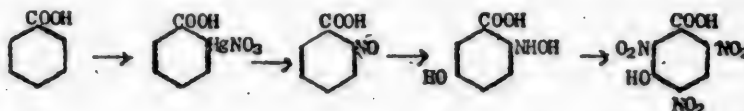


only the ortho isomers give nitroso compounds suitable for conversion under the conditions of the reaction into anomalous nitrophenols, that is, into trinitro-m-cresol and trinitro-m-chloro-

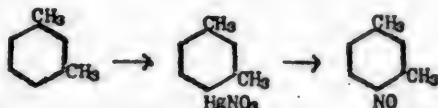
phenol respectively, in accordance with the experimental results.

Quite clear also are the causes for the formation during the catalytic nitration of toluene and chlorobenzene of significantly smaller quantities of nitrophenols than during the nitration of benzene, since the *p*-nitroso compounds formed from the *p*-mercury compounds, not being subjected to oxidative nitration according to equation (5), are almost completely transformed under these conditions into nitro compounds according to equation (3).

It now also becomes possible to comprehend the formation during the catalytic nitration of benzoic acid of 3-hydroxy-2,4,6-trinitro benzoic acid (9), if we take into account that the mercuration of benzoic acid gives an ortho compound:



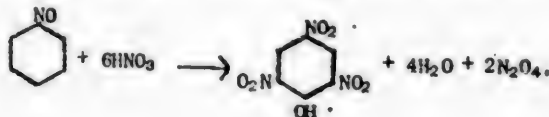
There is also no cause for perplexity in the almost complete lack of formation of nitrophenols in the catalytic nitration of *m*-xylene (10), as the arylmercury compound formed from it is transformed smoothly into nitrosoxylenes, whose para position with respect to the nitroso group is occupied:



and it must be almost completely transformed under the usual conditions of nitration into nitrosoxylenes. On the basis of our observations on the conversion under the action of nitric acid of nitro, nitroso, and mercury compounds solely into the corresponding dinitro compounds, it is easy to understand the causes for the lack of formation of nitrophenols during the catalytic nitration of nitrobenzene (7,11). The difficulty of mercuration of nitrobenzene explains the weak catalytic effect of mercury salts in this and similar cases.

The lack of significantly increased velocity of the reaction, and of the increased formation of nitrophenols from the addition salts of mercury in the nitration of naphthalene (12) can be ascribed to the fact that nitration of this hydrocarbon in the presence of oxides of nitrogen proceeds, in accordance with our previous work, very rapidly (13), with incomparably greater speed than its mercuration. The same thing, of course, is observed for other compounds which react rapidly with nitrogen dioxide, e.g., phenols and amines. In connection with this we must make the general observation that increased speed of reaction and increased formation of nitrophenols from addition salts of mercury during nitration can take place only for those compounds whose speed of mercuration under the given conditions is greater or at least on a level with the speed of direct reaction with nitrogen dioxide. It is clear that under comparable conditions (such as increased concentration of mercury salts and a smaller amount of nitric dioxide and acid) it is possible to obtain catalytic and specific effects from the addition salts of mercury.

All the other known experimental results of catalytic nitration in the presence of mercury salts correspond fully with the requirements of our theory. Thus, in the first communication, we pointed out the necessity for the presence of nitrogen oxides in the catalytic nitration of aromatic compounds as well as of their mercury derivatives. The consumption of nitrogen dioxide in the formation of nitroso compounds is later more than made up by the latter's oxidative nitration, in accordance with the stoichiometric equation.

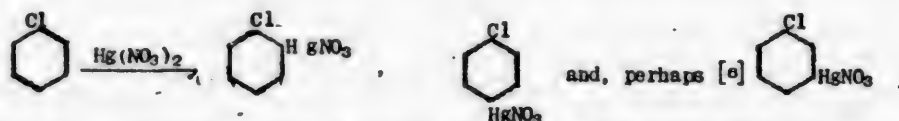




and also by collateral oxidation of the nucleus to oxalic acid and  $\text{CO}_2$ . Thus oxidative nitration in the presence of mercury salts appears to be a complicated series of catalytic processes, in which the role of accelerant is played by mercury salt and nitrogen dioxide, the further reaction having an autocatalytic character.

It is necessary, however, to point out that in comparing catalytic nitration in the presence of mercury salts and nitration under similar conditions of the corresponding mercury derivatives and nitroso compounds, in addition to their similarities, it is also necessary to take into account several differences in the course of the reactions, two of which we shall pause to consider. An extremely important characteristic of the usual conditions of catalytic nitration is the extraordinarily small concentration of intermediate mercury derivative, and consequently, of the nitroso compound formed from the latter. Because of this, bimolecular and still more complicated processes of polymerization according to an equation of type (6) are very improbable, which explains the lack of formation of colored products during the course of catalytic nitration under the usual conditions, and even at low temperature.

Another peculiarity of catalytic nitration is the fact that nitration takes place in the majority of cases with a mixture of isomeric mercury derivatives, formed during the mercuration of the original compound; for example, with chlorobenzene:



the relative proportions of these mercury compounds may be significantly different from the proportions of isomeric nitro compounds formed during the usual nitration, and even from the proportions of isomers in the products of mercuration. In the latter case, in view of the reversibility of mercuration, the formation of products of reaction will more or less correspond to the equilibrium between the isomers, just as in catalytic nitration the proportions of nitrated isomers will be determined only by the speed of their formation.

In conclusion, we express the sincere conviction that the results of our investigations as presented above will offer a hopeful starting point for the further fruitful study of the nitration of nitroso compounds, mercurio and several other metallo-organic derivatives, and also of the catalytic nitration of aromatic compounds. In this connection we may mention that predictions made on the basis of our theory concerning various new results in the field of catalytic nitration in the presence of mercury salts have been well confirmed by experimental verification. Thus we have shown, for example, that the mixture of nitrotoluenes formed by the catalytic nitration of toluene consists chiefly of the para isomer; that depending upon the conditions of the reaction, in the mixture of nitrocresols formed the o- or m-cresol derivative predominates; we have also demonstrated the formation under mild conditions of the diazo compound and dinitro-p-cresol.

#### EXPERIMENTAL

(Together with A. N. Barishnikova)

##### I. Combined action of concentrated nitric acid and nitrogen oxides upon nitro derivatives and para-substituted aryl mercury compounds

1. Experiments with p-tolyl mercury. To a mixture of 10 ml. of nitric acid, sp. g. 1.42, and 0.5 g. trioxymethylene, added for the formation of nitrogen oxides, there was gradually added in the course of 1 hour 30 minutes, with energetic stirring and a temperature of

-20°C an intimate mixture of 3 g. p-tolyl mercury and 0.5 g. trioxymethylene. After being maintained for one half hour at the indicated temperature, the reaction mixture was poured upon 30 g. of ice, and the greenish-brown sediment deposited filtered and washed with water. The sediment was then dissolved in ether, washed with weak alkali, dried over potash, and the solvent driven off. 1.3 g. of p-nitroso toluene were recovered -- 68% of theoretical. It quickly and completely distilled with steam, distilled in a manner characteristic of the nitro compound, and the colorless product obtained in this manner melted at 48°C to a green liquid, in accordance with the data for p-nitroso toluene.

The mother liquor from the p-nitroso toluene gave with an alkaline or acetic acid solution of  $\beta$ -naphthol the reaction for the p-tolyl diazo salt, and the solution of alkali used for washing, upon acidification, grew turbid, and revealed by its odor the presence of nitrocresols.

Upon conducting the reaction of p-tolyl mercury with nitric acid at 65°C, p-nitro-toluene was obtained in good yield. The same result was obtained if the reaction mixture was allowed to react below 0°C and then heated.

2. Experiments with p-tolyl mercury chloride. To a mixture of 15 ml. nitric acid, sp. g. 1.36, 2 g. of finely powdered silver nitrate and 0.3 g. trioxymethylene in the form indicated earlier, there was added in the course of 30 minutes and at a temperature of about 10°C a mixture of 3 g. p-tolylmercury chloride and 0.5 g. trioxymethylene. Upon working up the reaction mixture, there was obtained 1.0 g. of p-nitroso toluene, with a small admixture of p-nitrotoluene (about 90% of theoretical). In the mother liquid, the presence of diazo compound was determined in the manner indicated previously; no nitrocresol was found in the alkaline wash solution.

3. Experiments with p-chlorophenylmercury acetate. 0.8 g. mercury derivative was added to a mixture of 10 ml. nitric acid, sp. g. 1.36, and 0.3 g. trioxymethylene. The reaction at from 10-20°C lasted about two hours. After pouring on 30 g. ice, filtration, and steam distillation, there was obtained 0.22 g. of pure p-nitrosochlorbenzene, with a melting point of 87-88°C. It gave a sharp depression of the melting point in a combined melting point test with p-nitrosochlorbenzene. The yield of nitroso product was about 68% of theoretical; in the mother liquid the presence of diazo compounds was detected.

The formation of p-nitrosochlorbenzene, because of its comparatively great resistance to oxidation by nitrogen dioxide, can be successfully carried out even at a temperature of 20-30°C; upon raising the temperature to 60°C or higher, the reaction gives a good yield of p-nitrochlorbenzene. Under intermediate conditions, the reaction product consists of a mixture of nitroso- and nitro- compounds.

4. Experiments with m-nitrophenylmercury acetate. The reaction of nitro derivatives of arylmercury compounds with nitric acid containing oxides of nitrogen proceeds only under comparatively severe conditions as a result of the decrease in nucleophilic properties of the molecule in the presence of the nitro group. During the reaction, a significant part of the nitrosodinitro compound formed is oxidized to the corresponding dinitro compound. Thus, for example, the reaction of 3 g. m-nitrophenylmercuracetate with a mixture of 15 ml. nitric acid, sp. g. 1.4, and 0.5 g. trioxymethylene, in the course of 3 hours at 40°C gave a very good yield (2.3 g.) of a mixture of approximately equal quantities of m-nitrosodinitrobenzene and m-dinitrobenzene, which could be separated by steam distillation and subsequent recrystallization. In this case, the formation of nitrophenols was not observed.

## II. Combined action of dilute nitric acid and oxides of nitrogen upon mercuroaromatic compounds

The scheme of the course of the basic reaction is:



5. Experiments with phenylmercuracetate. Into a three-necked flask fitted with a stirrer and mercury seal, there were added 0.5 g. of mercurio derivative and 10 ml. nitric acid, sp. g. 1.2, and after the mixture was cooled to 0°C, pure nitric oxide was passed through it. The insoluble material dissolved rapidly and phenyldiazo nitrate was formed, whose yield upon titration with  $\beta$ -naphthol was close to the theoretical.

The solution of diazo salt in nitric acid was fairly stable. Only after many days of standing did crystals of 2,4-dinitrophenol begin to deposit -- a product of the conversion of the diazo compound into phenol, and the nitration of the latter. Upon heating, this reaction took place very rapidly.

6. Experiments with o- and m-chlorphenylmercuracetate. The material added consisted of 1 g. mercury derivative and 15 ml. nitric acid, sp.g. 1.2. The reaction of nitric oxide under these conditions took place with more difficulty than with phenylmercuracetate; at 45°C it was complete in 45 minutes.

The solution of o-chlorphenyldiazo nitrate was exceedingly stable, even upon heating, as could be seen from the following experiment. The solution of diazo compound obtained as indicated above was heated for 33 hours at 85°C. Upon cooling, there deposited 0.18 g. of pure 2,4-dinitro-6-chlorphenol, with a melting point of 110°C. From the mother compound, after precipitating the oxide of mercury with alkali and coupling with  $\beta$ -naphthene there were obtained 0.21 g. of azo dye with a melting point of 161-165°C, giving no depression of melting point in a mixed melting point test with the product of coupling o-chlorphenyldiazo chloride with  $\beta$ -naphthol. Thus, about 23.5% of o-chlorphenyldiazo nitrate remained unchanged after such long heating.

7. Experiments with m-chlorphenylmercuracetate. The material added consisted of 1.5 g. mercury derivative and 12 ml. nitric acid, sp.g. 1.2. After passing in nitric oxide at 0°C for one hour, no formation of diazo salt was observed. Upon raising the temperature to 20°C, the reaction was completed in 1.5 hours. The yield of diazo compound on titration with  $\beta$ -naphthol was 78% of theoretical.

8. Experiments with o-tolylmercury at low and high temperature [2]. The reaction at low temperature proceeded just as with phenylmercuracetate, with the formation of diazo compound. To carry out the reaction at a higher temperature, we proceeded as follows. 1 g. o-tolylmercury, well mixed with 0.3 g. trioxymethylene, was gradually, in the course of an hour, added with energetic stirring and a temperature of about 60°C, to a mixture of 25 ml. of nitric acid, sp. g. 1.1, and 0.1 g. trioxymethylene; the latter served for the formation of nitrogen oxides. After reacting for an hour at 60°C, the reaction mixture was distilled. The distillate, containing needlelike crystals, was extracted with ether, and the ether solution in its turn extracted with 3% alkali. Upon acidification of the alkaline solution, there were obtained 0.16 g. dinitro-o-cresol with a melting point of about 76°C; after recrystallization from alcohol, it was 83-84°C. In a mixed melting point test of the product with a known sample of dinitro-o-cresol (4,6-dinitro-2-methyl-1-hydroxybenzene) no depression of the melting point was observed.

After driving off the solvent from the ether extract, there was obtained about 0.1 g. of an oil which, to judge from the analogous experiment with o-nitrosotoluene, consisted chiefly of o-nitrotoluene. The residue in the flask, after hot filtration, gave an insoluble salt of mercury, probably the oxalate; no trinitro-m-cresol was observed in it (compare with the following results).

### III. Combined action of concentrated nitric acid and oxides of nitrogen on mercurioaromatic compounds with free para positions with respect to the mercury -- oxidative nitration of mercurioaromatic compounds

9. Oxidative nitration of o-tolylmercury. 2 g. of o-tolylmercury were sprinkled in the course of thirty minutes, with stirring, at a temperature of about 40°C, into 10 ml. of nitric acid, sp. g. 1.4, to which 0.2 g. trioxymethylene had been added. After a half hour



in a boiling water bath with 5 ml. of additional nitric acid, sp.g. 1.5, the reaction mixture was diluted with water, and steam distilled. The residue in the flask, after hot filtration gave 0.82 g. of pure trinitro-*m*-cresol with a melting point of 104-105°C, giving no depression of the melting point in a mixed test with known product.

The distillate was extracted with ether, which was then washed with 3% alkali. After driving off the solvent, 0.19 g. of raw *o*-nitrotoluene was obtained. Upon treating the alkaline extract in the usual way, 0.28 gm. nitrocresols were obtained, which after thorough treatment with nitric acid during heating gave an additional 0.23 g. of pure trinitro-*m*-cresol.

10. Oxidative nitration of *o*-chlorphenylmercuracetate. a). 3 g. *o*-chlorphenylmercuracetate were added in the course of 10 minutes at a temperature of 40-50°C to a mixture of 6 ml. nitric acid, sp.g. 1.38, and 0.1 gm. trioxymethylene. After an hour at 50°C, the cooled reaction mixture was brought by the addition of a 15% solution of caustic soda to an alkaline reaction, and the resulting precipitate filtered and washed.

Upon acidification of the alkaline solution, there was obtained 0.90 g. of pure 2,4-dinitro-*m*-chlorphenol, which after a single crystallization from alcohol melted at 89-90°C, and gave no depression of the melting point in a mixed test with known 4,6-dinitro-3-chlor-1-hydroxybenzene. The yield of dinitro-*m*-chlorphenol was 51% of theoretical. The mother filtrate, upon titration with  $\beta$ -naphthol, contained diazo compound in about 5% of the theoretically possible amount. The precipitate formed during the alkalization of the reaction mixture, consisting chiefly of mercuric oxide, was steam distilled. From the distillate there was obtained a small quantity of *o*-nitrochlorbenzene with a melting point of 29-31°C, identified by a mixed melting point test with known pure product.

Under similar conditions, 6 g. *o*-chlorphenylmercuracetate were nitrated for 5 hours at 50°C. 50 ml. water were added, and the resulting mixture steam distilled for a short time. From the distillate after alkalization there were obtained 0.70 g. *o*-nitrochlorbenzene with melting point of 32-33°C, 22% of theoretical, and a small quantity of dinitro-*m*-chlorphenol. From the residue in the distillation flask, after hot filtration of the tar (0.3 g.) there was obtained 1.3 g. of a mixture of dinitro- and trinitro-*m*-chlorphenols with a melting range of 104-120°C. After an hour's heating of this mixture on the water bath with nitric acid, sp. g. 1.5, it was converted into pure trinitro derivative, with a melting point of 113-115°C, identified by a mixed melting point test with pure 2,4,6-trinitro-*m*-chlorphenol.

b) Nitration according to Hanke's method [6]. 1 gm. *o*-chlorphenylmercuracetate was added with stirring in the usual apparatus in the course of a few minutes to 5 ml. of 68% nitric acid. During the following 30 minutes, the temperature of the mixture was raised to 65°C. After 10 minutes, the reaction product was cooled to the usual temperature, poured into 25 ml. water, neutralized with soda, and then steam distilled.

From the distillate a little *o*-nitrochlorbenzene was obtained. The residue in the flask, after hot filtration to remove turbidity and acidification, gave 0.18 g. dinitro-*m*-chlorphenol with a melting range of 76-86°C; after a single crystallization from water, it melted at 88-90°C. Neither before nor after recrystallization did the product give a depression of the melting point in a mixed test with known dinitro-*m*-chlorphenol.

11. Oxidative nitration of *m*-chlorphenylmercuracetate. 5.2 g. *m*-chlorphenylmercuracetate were gradually added at 50°C to 14 ml. nitric acid, sp.g. 1.37 and 0.3 g. trioxymethylene. After an hour at the same temperature, the reaction mixture was added to 40 ml. water and distilled for a short time with steam. After alkalization of the distillate, there was filtered off 0.6 g. *m*-nitrochlorbenzol with a melting point of 43-44°C, about 20% of theory. The residue in the distillation flask after filtration while hot and mixing with the aqueous alkaline part of the distillate gave upon cooling 2.6 g. of 4,6-dinitro *o* chlorphenol with a melting point of 110-111°C, 6% of theory.

The extremely smooth course of the oxidative nitration in this case completely corresponds to the results of our experiments on the study of the conversion under similar circumstances of *m*-nitrosochlorbenzol into dinitro-*o*-chlorphenol with a yield of 70% of the theor-



etically possible quantity.

12. Oxidative nitration of phenylmercuracetate. Experiments at the usual and higher temperatures were described earlier [1]. The general yield of all products, with the exception of oxalic acid, was about 60% of theoretical, of which 2% could be ascribed to nitrobenzene, 3% to p-dinitrobenzene, and the remaining 55% consisted of 2,4-dinitrophenol and picric acid.

Upon mixing in the course of an hour and at a temperature near 0°C, 3 g. phenylmercuracetate and 0.6 g. trioxymethylene with 15 ml. nitric acid, sp.g. 1.36, to which 0.3 g. trioxymethylene had been added, there was observed a strong darkening of the reaction mass. After an hour, the mixture was poured upon 60 g. of ice, and the dark precipitate formed was washed with water and ether. Of the dry precipitate, insoluble in the usual solvents, there was obtained 0.42 gm. Probably, judging from its nature, this product is analogous to the materials formed under similar conditions from nitrosobenzene and p-nitrosodiphenylhydroxylamine.

From the filtrate and the ether extract of the steam distillate about 0.5 g. of 2,4-dinitrophenol was recovered. The formation of diazo compound either during the initial reaction or later was not observed.

To everything said above, it is necessary to add that in accord with our previous experiments [1], mercurioaromatic compounds under the action of nitric acid up to a certain concentration (60%) and in the absence of nitrogen oxides undergo only a splitting into the corresponding aromatic compound and the nitrate of oxidized mercury. The mercury derivative, and also the nitroso compound under the action of nitrogen dioxide in an organic solvent in the absence of nitric acid and nitric oxide (as a result of conducting the reaction with agitation in an atmosphere of oxygen) is almost completely oxidized to the corresponding nitro compound according to equation (3).

As our present and our III communications were going to press, we learned of articles by American chemists (J. Am. Soc., 69, 773) in which are described results already reached in our work [1,2,3,4]. As the dates of reception of our previous communications [1,2,3,4] given in the Journ. Gen. Chem. (USSR) show, their contents, basic attainments in the field of discovery and research in the oxidative nitration of nitroso compounds and mercury derivatives, and an explanation of the mechanism of nitration in the presence of mercury salts, were first obtained by us. We wish to take the occasion to point out also that the basic mechanism of nitration with sulfuric-nitric mixtures through reaction with the nitroniumcation was given in our work (A Titov, Dissertation, 1941; Journ. Gen. Chem. (USSR) 18, 773, received by editor March 14, 1946) earlier than in the communications of Karasch, Bennett, Ingold and their co-workers.

#### CONCLUSIONS

1. On the basis of earlier reported results on the consecutive formation of intermediate mercury derivatives and nitroso compounds during the nitration of aromatic materials in the presence of mercury salts a thorough explanation has been given of the results of experimental study of this reaction.

2. It has been shown experimentally that during the nitration of mercurioaromatic compounds by nitric acid in the presence of oxides of nitrogen, nitroso compounds or products of their transformation are formed under conditions of reaction corresponding to equations (3) to (7) -- mononitro compounds, diazo compounds, normal and anomalous nitrophenols (oxidative nitration), p-nitrosodiphenylhydroxylamines and products of their change, and also p-dinitro compounds.

# LITERATURE CITED

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## ADDITION OF $\alpha$ -HALOGEN ETHERS TO BUTADIENE

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The investigation of the manner in which various reagents combine with compounds containing conjugated systems of double bonds, in the sense of primary 1,2 or 1,4 additions, is of considerable interest in organic chemistry. The answer to this question in any individual case may yield valuable information on the addition mechanism. The initial work done on the addition of halides and halogen hydracids to butadiene and its homologs by Thiele [1] and others led them to picture this as a direct 1,4 addition. In consequence of the later research done by Claisen [2], Prevost [3], and others on allyl rearrangements, however, many of the conclusions concerning the manner of addition that resulted from earlier work were questioned, while several of them were found to be false. Doubt was likewise cast upon the very method of the quantitative determination of the products of 1,2 and 1,4 addition, based upon the fractional distillation of the reaction products of the straight thermal isomerization of allyl halide derivatives. This was especially true of the allyl bromide derivatives, which have a very marked tendency toward isomerization, as has been demonstrated by the recent investigations of Young [4] and his associates. As for the chlorine derivatives, determination of the order of addition by the usual methods involving the analysis of the end products of the reaction appears to be a much more reliable procedure owing to the stability of allyl chloride isomers over rather wide ranges of temperature. However, as B. A. Arbuzov and one of the present authors [5] demonstrated, when the addition reaction of halogen reagents to butadiene is performed in the presence of catalysts, a new factor, previously unrecognized, must be taken into account: the catalytic isomerization of allyl halide compounds, which occurs with considerable velocity at temperatures in the 0--10°C range, i.e., at the temperatures at which the addition reactions are ordinarily effected and at which the thermal isomerization of allyl chloride isomers is practically absent.

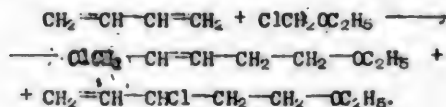
We demonstrated that when chloromethyl ether is added to butadiene in the presence of zinc chloride, the mixture obtained consists of 45% of the 1,2 and 55% of the 1,4 compounds. The data of the catalytic isomerization of the addition products enabled us to demonstrate that 75--80% of the actual addition products were in the 1,2 position, while 20-25% were in the 1,4. Our experimental data enabled us to take a critical stand toward the ionic theory of the addition of reagents to conjugated systems set forth by Ingold, Burton, and other representatives of the British school, and to conclude that the addition of chloromethyl ether to butadiene takes place, not ionically, but apparently as a molecular or a mixed ionic-molecular reaction.

It was the object of the present paper to confirm, extend, and develop the foregoing research by means of the addition reaction of chloromethyl ethyl ether, chloromethyl butyl ether, and chloromethyl isobutyl ether to butadiene. Special attention was to be given to a study of the catalytic isomerization of the addition products and to elucidation of the manner in which the indicated  $\alpha$ -halogen ethers were added to butadiene. The chloromethyl, chloromethyl isobutyl, and chloromethyl butyl ethers were synthesized in the usual manner: saturating hydrogen chloride with a mixture of polyoxymethylene and the corresponding alcohol.

The reactions of adding halogen ethers to butadiene were effected with cooling in the presence of 1% zinc chloride.

When chloromethyl ethyl ether was added to butadiene, two addition products were obtained:

1-ethoxy-3-chloropentene-4, with a b.p. of 28°C (3mm), a  $n_D^{20}$  of 1.4345, and a  $d_4^{20}$  of 0.9490; and 1-ethoxy-5-chloropentene-3, with a b.p. of 43°C (3mm), a  $n_D^{20}$  of 1.4310, and a  $d_4^{20}$  of 0.9707.



Of the mixture obtained, 53% was 1-ethoxy-3-chloropentene-4, and 4% was its isomer. The overall yield was 75% of the theoretical figure.

When chloromethyl isobutyl ether was added, three products were obtained: diisobutylformal, with a b.p. of 47-48°C (8 mm),  $n_D^{20}$  1.4020, and  $d_4^{20}$  = 0.8275; 1-isobutoxy-3-chloropentene-4, with a b.p. = 71°C (10 mm),  $n_D^{20}$  = 1.4350, and  $d_4^{20}$  = 0.9; and 1-isobutoxy-5-chloropentene-3, with a b.p. = 93-94°C (15 mm),  $n_D^{20}$  = 1.4460, and  $d_4^{20}$  = 0.9342.

The mixture obtained was fractionated with the eight-bulb dephlegmator designed by A.E. Arbuzov. The overall yield of isomeric isobutoxychloropentenes was 65%. The 1-isobutoxy-3-chloropentene-4 was 53% of the mixture. A yield of 12% of diisobutylformal was obtained, allowing for the chloromethyl isobutyl ether used in the reaction.

Analogous results were obtained when chloromethyl butyl ether was added to the butadiene. Repeated distillation of the reaction mixture obtained through a meter-high column packed with glass rings likewise yielded three products: 1-butoxy-3-chloropentene-4, with a b.p. = 77°C (9 mm),  $n_D^{20}$  = 1.4367, and  $d_4^{20}$  = 0.9260; dibutylformal, with a b.p. = 70°C (8 mm),  $n_D^{20}$  = 1.4040, and  $d_4^{20}$  = 0.8622; and 1-butoxy-5-chloropentene-3, with a b.p. = 93-94°C (9 mm),  $n_D^{20}$  = 1.4500, and  $d_4^{20}$  = 0.9461.

The yield and the proportion of the addition products were about the same as in the previous reaction. When we examine the addition reactions of butadiene with chloromethyl butyl and chloromethyl isobutyl ethers, the formation of acetals: diisobutyl and dibutyl formals, is worthy of note. The formation of diisobutyl and dibutyl formals may be considered to occur as follows: When the reaction products are treated with water, the halogen ether not entering into the reaction is hydrolyzed.



This hydrolysis differs from that of the chloromethyl and chloromethyl ethyl ethers in that it proceeds slowly and is incomplete. The alcohol formed reacts with the unhydrolyzed halogen ether to form an acetal.



In tests specially set up for the purpose it was found that no acetal is formed when pure chloromethyl ether is hydrolyzed. When chloromethyl ethyl ether is hydrolyzed, the acetal yield is 14%; when chloromethyl propyl ether is hydrolyzed, the dipropylformal yield is 65%; while when chloromethyl butyl and chloromethyl isobutyl ethers are hydrolyzed, the acetal yield is 70-80%. Acetals are likewise formed when halogen ethers are treated with dilute hydrochloric acid. The supposed method of formation of acetals in the reactions under investigation was finally confirmed by the action of an equimolecular quantity of butyl alcohol upon chloromethyl butyl ether -- a 91% yield of dibutylformal was obtained.

We effected the catalytic isomerization of ethoxychloropentenes and butoxychloropentenes by the method described in the preceding paper [5]. The isomerization was performed at the temperatures of -10°, 0°, and +17° C in the presence of zinc chloride. The amounts of zinc chloride used were 0.002, 0.006, and 0.01 moles per mole of the chloride. The degree of isomerization of the chlorides was computed from the refractive indices of the solutions, measured at fixed intervals of time. The results of the catalytic isomerization of ethoxychloropentenes at the temperature of +17° C are given in Fig. 1 and in Table 3, while the results for 0° are shown in Fig. 2 and Table 4.

Curves I, II, and III in Fig. 1 represent the isomerization of 1-ethoxy-3-chloropentene-4 for molar contents of zinc chloride of 0.002, 0.006, and 0.01, respectively, while Curve IV denotes the isomerization of 1-ethoxy-5-chloropentene-3 for 0.01 mole of zinc chloride per mole of chloride.



In Fig. 2 Curves I and II represent the isomerization of 1-ethoxy-3-chloropentene-4 with 0.006 and 0.01 moles of zinc chloride, while Curve III shows the isomerization of 1-ethoxy-5-chloropentene-3 with 0.01 mole.

Figure 3 and Tables 5 and 6 illustrate the catalytic isomerization of pure butoxy-chloropentenes and their mixtures at 17°C, while isomerization at 0°C is shown in Fig. 4 and Table 7.

In both figures, Curves I and II represent the isomerization of secondary butoxy-chloropentene with 0.006 and 0.01 moles of zinc chloride per mole of chloride, while Curves III and IV indicate the isomerization of mixtures of chlorides, and Curve V indicates the isomerization of primary chloride in the presence of 0.01 mole of zinc chloride.

Investigation of the catalytic isomerization of secondary ethoxychloropentene and butoxychloropentene at -10°C indicated that when the amount of zinc chloride present was 0.006 mole, 7-8% of the chloride was isomerized in two days; no appreciable isomerization was observed when the zinc chloride present constituted 0.002 mole per mole of chloride.

The graphs and tables indicate that the velocity of isomerization of chlorides increases with temperature and higher concentrations of the catalyst.

As for the velocity of isomerization of various chlorides at the same temperature and with equimolecular catalyst content, the graphs and tables show that in most cases the variation is only slight. The observed divergences of the curves is chiefly explainable, apparently, by a certain irregular course of the isomerization process during the initial period of time, since the dissolution of the zinc chloride in the chlorides takes place slowly (up to 10 hours or more) and requires periodic stirring.

In the state of equilibrium 74-75% constitutes primary methoxypentene, while 85-86% constitutes butoxychloropentene, both in terms of the isomers. The results obtained justify us in assuming that the substituting groups R may be arranged in the following order in compounds of the type  $R-CHCl-CH=CH_2$ , according to their activating influence upon the position of equilibrium:



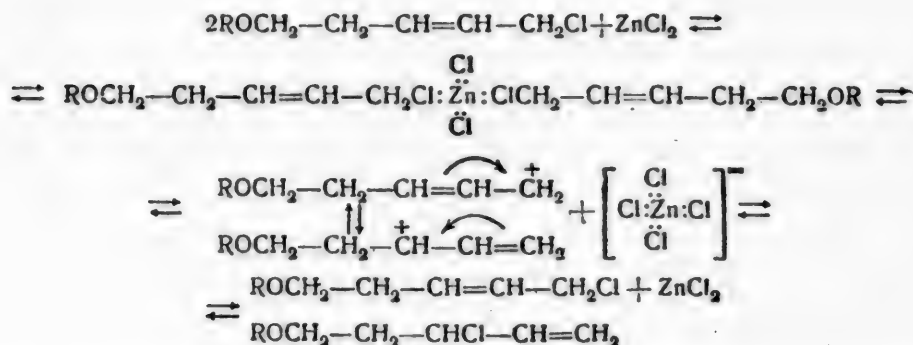
Table 1

Addition of Chloromethyl Ethyl Ether to Butadiene

Experiment No.	Percent of zinc chloride	Temperature of reaction, °C	$n_D^{20}$ of the distillate	Percent		actual percent of addition products in the 1,4 position.
				1-ethoxy-5-chloropentene-3 in the distillate	Isomerization of 1-ethoxy-3-chloropentene-4 under the reaction conditions	
1	0.55	-10	1.4410	39.4	8	31.4
2	0.18	-10	1.4400	33.3	-	33.3
3	0.55	+10	1.4410	39.4	8	31.4
4	0.18	-10	1.4385	24.2	-	24.2
5	0.55	+17	1.4422	46.6	17.0	29.6
6	0.55	0	1.4420	45.4	10	35.4

The data for the catalytic isomerization of ethoxy- and butoxy-chloropentenes permit us to arrive at definite conclusions concerning the order of addition of chloromethyl ethyl and chloromethyl butyl ethers to butadiene. According to the theory of Ingold and Burton [c].

the addition of halogen derivatives to the dienes takes place ionically; the addition is preceded by the polarization of the diene and the dissociation of the halogen derivatives into ions. Inasmuch as the mechanism of catalytic isomerization assumed by us [5]



likewise includes a stage of the addition of the chlorine ion to the electromeric form of the general ion, the reaction between the chloromethyl ethyl and chloromethyl butyl ethers and the butadiene, as postulated by Ingold and Burton, should give rise to a mixture containing 85-86% of primary and 14-15% of secondary chlorides. In practice, as we have seen, 45-55% of the mixture constitutes secondary chlorides. Inasmuch as

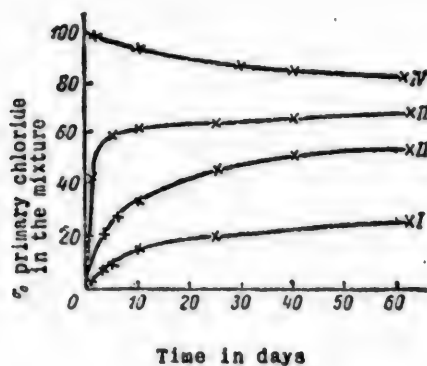


Fig. 1.

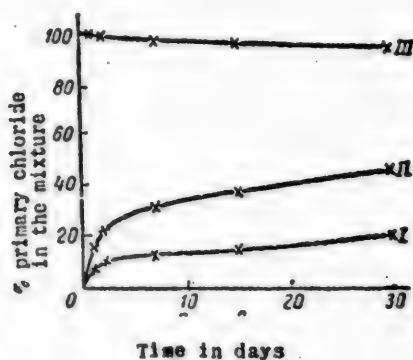


Fig. 2.

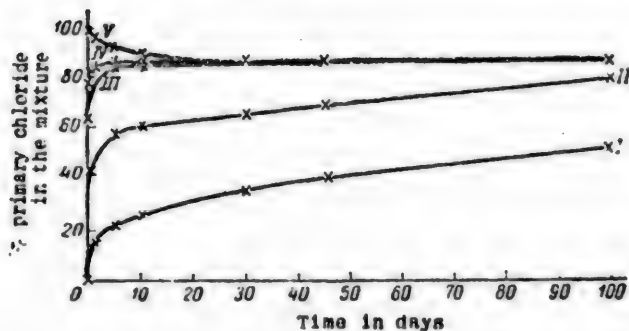


Fig. 3.

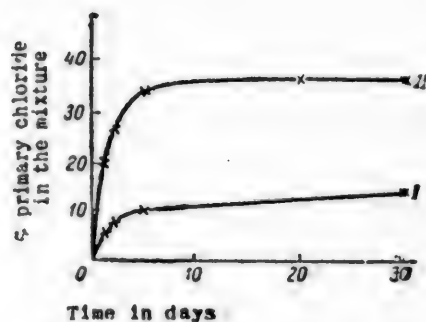


Fig. 4.

part of the secondary chloride is isomerized into the primary during the reaction, it is obvious that even more of the secondary must be formed at the instant of addition. Special tests were run in tubes, with varying quantities of zinc chloride and at various temperatures, to determine the actual course of the addition of chloromethyl ethyl and chloromethyl butyl ethers to butadiene. The reaction was continued for two days. Corrections from tabular data were applied to the isomerization of the secondary chlorides under the test conditions. The results obtained for the addition of chloromethyl ethyl ether to butadiene are given in Table 1, with the corresponding data for chloromethyl butyl ether given in Table 2.

TABLE 2  
Addition of Chloromethyl Butyl Ether to Butadiene

Experiment No.	Percent of Zinc Chloride	Temperature of reaction °C	$n_D^{20}$ of the distillate	Percent		Actual percent of addition products in the 1,4 position
				1-butoxy-5-chloropentene-3 in distillate	Isomerization of 1-butoxy-3-chloropentene-4 under the reaction conditions	
1	0.16	0	1.4427	45.1	5.5	39.6
2	0.46	0	1.4430	47.3	7.5	39.8
3	0.80	0	1.4439	54.1	26.3	27.8
4	0.16	-10	1.4413	34.5	0	34.5
5	0.46	-10	1.4424	42.9	6.9	36.0

According to Tables 1 and 2, when chloromethyl ethyl and chloromethyl butyl ethers are added to butadiene under the test conditions, 28-35% does so in position 1,4 and 65-72% in position 1,2. These figures agree with the results previously obtained by us for the addition of chloromethyl ether to butadiene.

#### EXPERIMENTAL

##### Adding Monochloromethyl Ethyl Ether to Butadiene

Into a thick-walled flask containing 160 g. of butadiene (95%), bedded in a freezing mixture, there was poured 260 g. of chloromethyl ethyl ether, cooled to  $-15^{\circ}\text{C}$ , after which 4 g. of freshly fused zinc chloride, ground to a powder, was added. The flask was sealed by a rubber stopper. A glass tube passed through the stopper and was fitted with a rubber tube equipped with a clamp. The stopper was wired fast to the neck of the flask. The contents of the flask were gently stirred, after which the flask was placed in a pan of ice for 10 to 15 hours and then allowed to stand for 10 to 15 hours at room temperature. The end of the reaction was indicated by a drop in the pressure within the flask; this could be easily ascertained by loosening the clamp on the rubber tube. After the reaction was completed, the reaction mixture was diluted with 200-300 ml. of ether and washed three times in a separatory funnel. When the ether solution was energetically shaken up with water, its color turned from brown to yellow. The layer of ether was dried with calcium chloride, the ether driven off on a water bath, and the residue fractionated under vacuum with the eight-bulb dephlegmator designed by A.E. Arbuzov. We obtained 170 g. of 1-ethoxy-3-chloropentene-4.

B. p.  $28^{\circ}\text{C}$  (3 mm),  $n_D^{20}$  1.4345,  $d_4^{20}$  0.9490.

Found:  $\text{MR}_D$  40.56.

$\text{C}_7\text{H}_{13}\text{OCl}$   $\text{F}_1$ . Calculated:  $\text{MR}_D$  40.83.

0.0940 g. substance: 0.091 g.  $\text{AgCl}$ .

Found %: Cl 23.8.

$\text{C}_7\text{H}_{13}\text{OCl}$ . Calculated %: Cl 23.9.

and 150 g. of 1-ethoxy-5-chloropentene-3:

B.p. 43°C (3mm),  $n_D^{20}$  1.4510,  $d_4^{20}$  0.9707.

Found:  $M_R^D$  41.21.

$C_7H_{13}OCl$   $F_1$ . Calculated:  $M_R^D$  41.83.

0.1213 g. substance: 0.117 g. AgCl.

Found %: Cl 23.8.

$C_7H_{13}OCl$ . Calculated %: Cl 23.9.

#### Adding Chloromethyl Butyl Ether to Butadiene

The chloromethyl butyl ether was prepared from anhydrous hydrogen chloride, polyoxymethylene, and butyl alcohol. Yield: 80-85%. A total of 825 g. of chilled chloromethyl butyl ether, together with enough zinc chloride to total 1% by weight of the reaction mixture, was poured into four thick-walled flasks containing a total of 370 g. of butadiene chilled to -15°C. The reaction and the subsequent treatment of the reaction mixture were effected in accordance with the method described in the preceding tests. Fractional distillation of the reaction mixture in a meter-high column packed with glass rings yielded 56 g. of dibutylformal:

b.p. 70°C (8 mm),  $n_D^{20}$  1.4040,  $d_4^{20}$  0.8622.

400 g. of 1-butoxy-3-chloropentene-4:

b.p. 77°C (9mm),  $n_D^{20}$  1.4367,  $d_4^{20}$  0.9260.

Found:  $M_R^D$  49.90

$C_9H_{17}OCl$   $F_1$ . Calculated:  $M_R^D$  49.80.

0.1111 g. substance: 0.0878 g. AgCl.

Found %: Cl 19.56.

$C_9H_{17}OCl$ . Calculated %: Cl 20.11.

and 385 g. of 1-butoxy-5-chloropentene-3:

b.p. 93-94°C (9 mm),  $n_D^{20}$  1.4500,  $d_4^{20}$  0.9461.

Found:  $M_R^D$  50.13.

$C_9H_{17}OCl$   $F_1$ . Calculated:  $M_R^D$  49.80.

0.1228 g. substance: 0.0944 g. AgCl.

Found %: Cl 20.04

$C_9H_{17}OCl$ . Calculated %: Cl 20.11.

The residue was a thick black fluid.

#### Adding Chloromethyl Isobutyl Ether to Butadiene

The reaction was effected with 109 g. of butadiene, 235 g. of chloromethyl isobutyl ether, and 3.4 g. of freshly fused zinc chloride that had been ground to powder. The method employed for the reaction and for the subsequent treatment of the reaction mixture was as described for the previous tests. Fractional distillation of the reaction mixture yielded 36 g. of diisobutylformal:

b.p. 50-51°C (10 mm),  $n_D^{20}$  1.4035,  $d_4^{20}$  0.8274.

Found:  $M_R^D$  47.19.

$C_6H_{12}O_2$ . Calculated  $M_R^D$  47.05.

122 g. of 1-isobutoxy-3-chloropentene-4:

b.p. 71°C, (10 mm),  $n_D^{20}$  1.4350,  $d_4^{20}$  0.9146.

Found:  $M_R^D$  50.20.

$C_9H_{17}OCl$   $F_1$ . Calculated:  $M_R^D$  49.80.

0.125 g. substance: 0.197 g. AgCl.

Found %: Cl 20.9

$C_9H_{17}OCl$ . Calculated %: Cl 20.11.

and 108 g. of 1-isobutoxy-5-chloropentene-3:

b.p. 93-94°C (15 mm),  $n_D^{20}$  1.4460,  $d_4^{20}$  0.9342.

Found:  $M_R^D$  50.24.

$C_9H_{17}OCl$   $F_1$ . Calculated:  $M_R^D$  49.80.

0.1437 g. substance: 0.1171 g. AgCl.

Found %: Cl 20.18.

$C_9H_{17}OCl$ . Calculated %: Cl 20.11.



#### Hydrolysis of Monochlorodimethyl Ether

A mixture of 20 g. of monochlorodimethyl ether and 22 g. of water was vigorously shaken for 10 minutes. It was noticed that the mixture grew warm. The mixture was then extracted with ether. No residue was found in the flask after the ether had been driven off.

#### Hydrolysis of Chloromethyl Ethyl Ether

To 15 g. of chloromethyl ethyl ether there was added 20 g. of water, after which the mixture was agitated for 15 minutes; the mixture was observed to grow warm. The mixture was then extracted with ether. The ether extract was desiccated with calcium chloride. The ether was driven from the flask to a Widmer dephlegmator, and the residue distilled from a small Arbusov flask. We obtained 1.1 g. of diethylformal with a b.p. of 87-89°C and a  $n_D^{20}$  of 1.3699.

#### Hydrolysis of Chloromethyl Propyl Ether

A mixture of 10 g. of chloromethyl propyl ether and 12 g. of water was vigorously agitated for 1.5 hours. The mixture was then extracted with ether. The residue left after desiccation and driving off the ether was distilled. We obtained 4.2 g. of dipropylformal with a b.p. of 136-137°C and a  $n_D^{20}$  of 1.3920.

#### Hydrolysis of Chloromethyl Butyl Ether

A mixture of 15 g. of chloromethyl butyl ether and 15 g. of water was agitated for two hours. No heating of the mixture was observed. The mixture was extracted with ether. The ether extract was desiccated with calcium chloride, the ether driven off, and the residue distilled in a small flask with a Widmer dephlegmator. We obtained 6.8 g. of di-n-butylformal with a b.p. of 179-180°C and a  $n_D^{20}$  of 1.4045.

#### Hydrolysis of Chloromethyl Butyl Ether by 5% Hydrochloric Acid

25 g. of chloromethyl butyl ether was agitated for 1.5 hours with 36 g. of 5% hydrochloric acid. The mixture was given the same treatment as in the preceding tests. We obtained 10.1 g. of di-n-butylformal with a b.p. of 180-181°C and a  $n_D^{20}$  of 1.4045.

#### Action of Chloromethyl Butyl Ether upon Butyl Alcohol

12.3 g. of chloromethyl butyl ether and 7.4 g. of butyl alcohol were shaken together in the agitator for four hours. The reaction mixture was distilled in a small flask with a Widmer dephlegmator. We obtained 14.7 g. of dibutylformal with a b.p. of 179-180°C and a  $n_D^{20}$  of 1.4049.

#### Catalytic Isomerization of the Ethoxychloropentenes

Experimental research on catalytic isomerization yielded ethoxypentenes possessing following constants:

1-ethoxy-3-chloropentene-4, b.p. 28°C (3mm),	$n_D^{20}$ 1.4345,	$d_4^{20}$ 0.9490.
1-ethoxy-5-chloropentene-3, b.p. 43°C (3 mm),	$n_D^{20}$ 1.4510,	$d_4^{20}$ 0.9707.

Some 2-3 g. of chloride were placed into small flat-bottomed flasks fitted with ground glass stoppers, after which the flasks were weighed. Freshly fused zinc chloride, ground to powder, was then added, and after reweighing, the mixtures were adjusted by adding chloride or zinc chloride to produce a solution of the desired concentration. The weighing was done on analytical balances. The flasks were then securely stoppered and allowed to stand at a given temperature. After a certain interval of time the refractive indices of the mixtures were determined, and from these values the percentage of chlorides in the mixtures was computed. It was determined in special experiments that the presence of dissolved zinc chloride had practically no effect upon the indices of refraction of the chloride mixtures.

Table 3

Isomerization of Ethoxychloropentenes in the Presence of  $\text{ZnCl}_2$  at  $+17^\circ\text{C}$ 

Elapsed time from beginning of isomerization (days)	1-Ethoxy-3-chloropentene-4						1-Ethoxy-5-chloropentene-3	
	0.18% $\text{ZnCl}_2$ (0.002 gr-mol)		0.55% $\text{ZnCl}_2$ (0.006 gr-mol)		0.92% $\text{ZnCl}_2$ (0.01 gr-mol)		0.92% $\text{ZnCl}_2$ (0.01 gr-mol)	
	$n_D^{20}$	Per cent isomerization of the chloride	$n_D^{20}$	Per cent isomerization of the chloride	$n_D^{20}$	Per cent isomerization of the chloride	$n_D^{20}$	Per cent isomerization of the chloride
1	1.4350	3.0	1.4370	15.1	1.4417	43.7	-	-
2	-	-	1.4373	17.0	-	-	-	-
3	1.4358	7.9	1.4378	20.0	1.4440	57.5	1.4508	1.3
5	1.4362	10.3	1.4391	28.1	1.4441	58.2	-	-
10	1.4370	15.1	1.4400	33.7	1.4446	61.2	1.4498	7.2
25	1.4380	21.2	1.4418	44.3	1.4451	64.2	1.4486	14.5
40	-	-	1.4430	51.5	1.4453	65.4	1.4483	16.3
63	1.4387	25.4	1.4434	53.9	1.4456	67.3	1.4480	18.1

The first series of experiments was carried out at a temperature of  $+17^\circ\text{C}$ . The results obtained are listed in Table 3.

The data for the catalytic isomerization of ethoxychloropentenes at  $0^\circ\text{C}$  are shown in Table 4.

The isomerization of 1-ethoxy-3-chloropentene-4 at  $-10^\circ\text{C}$  was continued for two days. With 0.55% of zinc chloride about 8% of the chloride was isomerized; with 0.18% of zinc chloride practically no isomerization occurred.

Table 4

Isomerization of Ethoxychloropentenes in the Presence of  $\text{ZnCl}_2$  at  $0^\circ\text{C}$ 

Elapsed time from beginning of isomerization (days)	1-Ethoxy-3-chloropentene-4				1-Ethoxy-5-chloropentene-3	
	0.55% $\text{ZnCl}_2$ (0.006 gr-mol)		0.92% $\text{ZnCl}_2$ (0.01 gr-mol)		0.92% $\text{ZnCl}_2$ (0.01 gr-mol)	
	$n_D^{20}$	Per cent isomerization of the chloride	$n_D^{20}$	Per cent isomerization of the chloride	$n_D^{20}$	Per cent isomerization of the chloride
1	1.4356	6.7	1.4369	14.5	1.4509	0.6
2	1.4361	10.0	1.4379	20.6	1.4508	1.3
3	1.4364	11.5	1.4496	30.9	1.4504	3.7
15	1.4368	13.9	1.4405	36.4	1.4502	5.0
30	1.4376	18.8	1.4416	43.0	1.4495	9.0

#### Catalytic Isomerization of Butoxychloropentenes

For the complete removal of dibutylformal from butoxychloropentenes the latter were treated with 5% hydrochloric acid for 20 hours, with vigorous stirring.\*

\* We noted that when butoxychloropentenes are treated with dilute hydrochloric acid they are partially isomerized.

The catalytic isomerization was performed on butoxychloropentenes possessing the following constants: 1-butoxy-3-chloropentene-4, b.p. 77°C (9 mm),  $n_D^{20}$  1.4367,  $d_4^{20}$  0.9260, and 1-butoxy-5-chloropentene-3, b.p. 93-94°C (9 mm),  $n_D^{20}$  1.4500,  $d_4^{20}$  0.9461. The isomerization was effected in the same manner as in the previous experiments.

TABLE 5

Isomerization of Butoxychloropentenes in the Presence of  $ZnCl_2$  at +17°C.

Elapsed time from beginning of isomerization (days)	1-Butoxy-3-chloropentene-4		1-Butoxy-3chloropentene-4		1-Butoxy-5-chloropentene-3	
	0.4% $ZnCl_2$ (0.006 gr-mol)		0.8% $ZnCl_2$ (0.01 gr-mol)		0.8% $ZnCl_2$ (0.01 gr-mol)	
	$n_D^{20}$	Per cent isomerization of the chloride	$n_D^{20}$	Per cent isomerization of the chloride	$n_D^{20}$	Per cent isomerization of the chloride
1	1.4392	18.7	1.4424	42.8	1.4496	3
5	1.4397	22.5	1.4445	58.6	1.4490	7.5
10	1.4403	26.8	1.4448	60.9	1.4487	9.8
30	1.4411	33.4	1.4454	65.4	1.4483	12.7
45	1.4426	44.3	1.4462	71.4	1.4483	12.7
100	1.4438	53.2	1.4474	80.4	1.4483	12.7

The data on the isomerization of pure butoxychloropentenes at +17°C are given in Table 5, and those for the isomerization of mixtures in Table 6.

Table 7 gives the data on the isomerization of 1-butoxy-3-chloropentene-4 at 0°C.

The isomerization of 1-butoxy-3-chloropentene-4 at -10°C was effected with 0.16% and 0.46% zinc chloride for a period of 2 days. No isomerization was observed for the first concentration, while 6.9% of chloride was found for the second.

TABLE 6

Isomerization of Mixtures of Butoxychloropentenes in the Presence of  $ZnCl_2$  at +17°C

Elapsed time from beginning of isomerization (days)	Input mixture:		Input Mixture:	
	$n_D^{20}$ 1.4455;	0.8% $ZnCl_2$	$n_D^{20}$ 1.4472;	0.8% $ZnCl_2$
	$n_D^{20}$	Percentage of 1-butoxy-5-chloropentene-3	$n_D^{20}$	Percentage of 1-butoxy-5-chloropentene-3
1	1.4476	81.9	1.4481	85.7
5	1.4479	84.2	1.4482	86.4
10	1.4480	85	1.4482	86.4
30	1.4481	85.7	1.4482	86.4
45	1.4481	85.7	1.4482	86.4
100	1.4481	85.7	1.4482	86.4

TABLE 7

Isomerization of 1-Butoxy-3-chloropentene-4 in the Presence of  $ZnCl_2$  at 0°C

Elapsed time from beginning of isomerization (days)	0.46% $ZnCl_2$ (0.006 gr-mol.)		0.8% $ZnCl_2$ (0.01 gr-mol.)	
	$n_D^{20}$	Percent isomerization of the chloride	$n_D^{20}$	Percent isomerization of the chloride
1	1.4374	5.2	1.4393	19.5
2	1.4377	7.5	1.4402	26.3
5	1.4381	10.5	1.4411	33.0
20	1.4382	11.3	1.4416	36.8
30	1.4385	13.5	1.4417	37.6

Addition of Chloromethyl Ethyl and Chloromethyl Butyl Ethers to Butadiene  
at Various Temperatures and Concentrations of Zinc Chloride

Equimolecular quantities of butadiene and the halogen ether, chilled to  $-15^{\circ}\text{C}$ , together with a computed amount of zinc chloride, were poured into glass tubes embedded in a freezing mixture. The tubes were sealed and left to stand at a given temperature for two days, being agitated at periodic intervals. Then the tubes were opened, and their contents treated with water and ether. The ether extract was desiccated with calcium chloride. After the ether was driven off, the mixture of chlorides was distilled in vacuum. The indices of refraction of the distillates were measured, and from these indices the percentage isomerization of the secondary chloride was computed. The corresponding corrections, taken from the tabular data given above, were then applied to the catalytic isomerization of the chlorides under the experimental conditions. The results are given in Tables 1 and 2.

CONCLUSIONS

1. The addition of chloromethyl ethyl, chloromethyl butyl, and chloromethyl isobutyl ethers to butadiene was investigated. The 1,2 and 1,4 addition products were separated and their constants determined.
2. It was shown that the hydrolysis of alpha halogen ethers takes place variously, depending upon the molecular weight of the halogen ether radical. Chloromethyl ether is completely hydrolyzed to formaldehyde, hydrogen chloride and alcohol. Hydrolysis of the chloromethyl ethyl, chloromethyl propyl, chloromethyl butyl, and chloromethyl isobutyl ethers yields the corresponding acetals; the mechanism of their formation is suggested and demonstrated.
3. The isomerization of ethoxychloropentenes and butoxychloropentenes was studied at various temperatures and concentrations of zinc chloride.
4. It was shown that chloromethyl ethyl and chloromethyl butyl ethers are added to butadiene in the 1,4 position in proportions ranging from 28% to 35%. The addition of alpha halogen ethers to butadiene does not occur ionically, but iono-molecularly or, possibly, molecularly.

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## THE SYNTHESIS OF BUTYLISOPROPYLACETYLENE

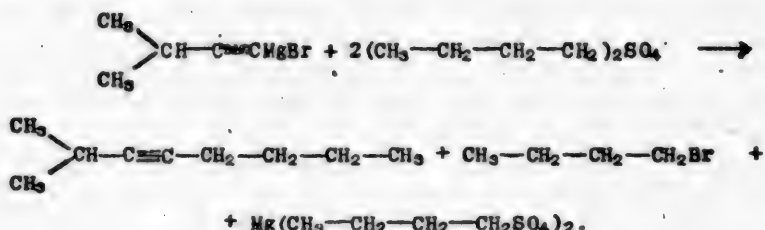
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The methods of producing dialkylacetylenes fairly rapidly by the action of dialkyl sulfates upon an alkylacetylene magnesium bromide, using the widely known and easily available dimethyl and diethyl sulfates, have been worked out by Thorn, Hennion, and Niewland [1]. We employed this method to produce methylisopropylacetylene and ethylisopropylacetylene. [2].

In the present paper this same method is used to produce butylisopropylacetylene, hitherto unknown in the literature, from isopropylacetylene magnesium bromide and butyl sulfate.

Without touching on the problem of the intermediate stages, the reaction may be expressed by the following equation:



The output of butylisopropylacetylene, purified by repeated fractional distillation, is 14% of the theoretical value. This hydrocarbon is a colorless, mobile liquid, with a somewhat sharp odor characteristic of acetylene hydrocarbons and a b.p. of 143-145°C.

Oxidation with a 5% solution of  $\text{KMnO}_4$  converts the hydrocarbon into isobutyric and valeric acids.

### EXPERIMENTAL

Isopropylacetylene is prepared by the method cited in the paper on the production of methyl-isopropylacetylene [2]. The butyl sulfite and butyl chlorosulfonate required for the synthesis of butyl sulfate were prepared by the method of Levaillant [3].

**Preparation of butyl sulfite.** 360 g. of thionyl chloride ( $\text{SOCl}_2$ ) were placed in a round-bottom flask fitted with a reflux condenser and a dropping funnel. After chilling, 444 g butyl alcohol was allowed to drop into the flask, after which the reaction mass was set aside at room temperature for a few hours and then gradually heated to 90-95°C, gaseous  $\text{HCl}$  being liberated. The butyl sulfite obtained was distilled at 114°C and 18 mm. The yield was 78% of theoretical.

**Preparation of butyl chlorosulfonate.** Chilled butyl alcohol (74 g.) was added to 135 g. of chilled sulfuryl chloride ( $\text{SO}_2\text{Cl}_2$ ). Dry air was passed through the reaction mass to agitate it and to remove the  $\text{HCl}$  formed. The final traces of  $\text{HCl}$  were removed by connecting the reaction flask to a water-jet pump.

**Preparation of butyl sulfate.** Since, according to Levailant [4], the isolation of butyl chlorosulfonate in a pure state is unnecessary for the preparation of butyl sulfate from it, it was directly converted from the crude into butyl sulfate. Butyl chlorosulfonate (crude) was slowly dropped into 175 g. of butyl sulfite during a period of 5 hours. The reaction was catalyzed by a slight quantity of  $\text{ZnCl}_2$ . The reaction mass was then chilled and washed with a 1% alkali solution and with water. The top layer was removed, and the aqueous layer was extracted with ether. The ether extract was added to the basic product and dried over  $\text{Na}_2\text{SO}_4$ . After filtration, the ether was driven off at a pressure reduced by 25-30 mm., while the dibutylsulfate was distilled at a pressure reduction of 4-5 mm. Dibutylsulfate with a b.p. of  $118^\circ\text{C}$  at 5.5 mm. was employed for the synthesis of butylisopropylacetylene. The yield was 68% of theoretical.

$d_4^{22}$  1.063;  $n_D^{22}$  1.4219;  $M_{\text{R}_D}$  50.19.  
 $\text{C}_9\text{H}_{18}\text{O}_4\text{S}$ . Calculated  $M_{\text{R}_D}$ : 50.129.

The synthesis of butylisopropylacetylene was effected under the conditions set forth by Thorn, Hennion, and Niewland [1]. A total of 48.2. of isopropylacetylene (b.p.  $28-28.5^\circ\text{C}$ ), diluted with an equal quantity of absolute ether, was added drop by drop to ethyl magnesium bromide, prepared in the usual manner from 17.23 g. of magnesium and 77.2 g. of ethyl bromide, the reaction mass being mechanically stirred and chilled at intervals. The reaction product was allowed to stand overnight and then heated until the mass simmered for 2.5 hours with constant stirring.

389 g. of butyl sulfate, diluted with absolute ether, was added drop by drop to the isopropylacetylene magnesium bromide thus prepared, after which the reaction mass was boiled for 12 hours. After the ether was carefully removed by means of a needle dephlegmator 0.75 m. high, the pasty mass left in the flask was treated with chilled dilute  $\text{HCl}$ . A layer of organic matter separated out; it was washed with water and then with a 20% solution of  $\text{NaOH}$ , desiccated over calcium chloride, and subjected to fractional distillation. The following fractions were obtained (in grams) after three fractionations:

I	b.p. $32-36^\circ\text{C}$	4	
II	b.p. $36-74$	2	
III	b.p. $74-95$	3	
IV	b.p. $95-99$	7.5	(bulk at $98-99^\circ\text{C}$ )
V	b.p. $99-100$	21	
VI	b.p. $101-103$	16	
VII	b.p. $103-106$	9	
VIII	b.p. $106-141$	4	
IX	b.p. $141-142$	1	
X	b.p. $142-145$	10.5	
XI	The residue of 5 g. did not distill without decomposition.		

The first two fractions yielded precipitates with an alcoholic solution of silver nitrate and bleached  $\text{KMnO}_4$ ; the fraction with a b.p. of  $95-99^\circ\text{C}$  had a  $n_D^{20}$  of 1.426; the fraction with a b.p. of  $99-101^\circ\text{C}$  had a  $n_D^{20}$  of 1.4352 and a  $d_4^{20}$  of 1.2274; while the fraction with a b.p. of  $101-103^\circ\text{C}$  had a  $n_D^{20}$  of 1.4368 and a  $d_4^{20}$  of 1.2415.

According to the literature, butyl bromide has a b.p. of  $101^\circ\text{C}$  and a  $d_4^{20}$  of 1.305. It must be assumed that the 95-103 fraction consists chiefly of butyl bromide.

The  $142-145^\circ\text{C}$  fraction, which constituted 14.3% (in terms of the input isopropylacetylene) represents butylisopropylacetylene, to judge by analysis and the oxidation products.

$d_4^{25.5}$  0.7665;  $n_D^{25.5}$  1.4182;  $M_{\text{R}_D}$  40.87.  
 $\text{C}_9\text{H}_{18}$ . Calculated:  $M_{\text{R}_D}$  41.09.  
 0.2552 g. substance: 0.8125 g.  $\text{CO}_2$ ; 0.3000 g.  $\text{H}_2\text{O}$ .  
 Found %: C 86.83; H 13.04.  
 $\text{C}_9\text{H}_{18}$ . Calculated %: C 87.1; H 12.9.

Oxidation of the 142-145°C fraction. A 5% solution of  $\text{KMnO}_4$  was added to 2 g. of the hydrocarbon until the coloration no longer disappeared. No neutral volatile products were observed with steam. The filtrate, after the removal of the  $\text{MnO}_2$ , was acidified with  $\text{H}_2\text{SO}_4$  and distilled. The four fractions collected were converted into silver salts and analyzed.

When the first fraction was boiled with freshly precipitated silver hydroxide, crystals separated out:

0.1085 g. of substance: 0.0590 g. Ag.

Found %: Ag 54.37.

$\text{C}_4\text{H}_7\text{O}_2\text{Ag}$ . Calculated %: Ag 55.38.

The third fraction, converted into a silver salt, yielded:

0.0936 g. of substance: 0.0480 g. Ag.

Found %: Ag 51.12.

$\text{C}_5\text{H}_9\text{O}_2\text{Ag}$ . Calculated %: Ag 51.58.

The fourth fraction, converted into a silver salt, yielded:

0.1074 g. of Substance: 0.0558 g. Ag.

Found %: Ag 51.95.

$\text{C}_5\text{H}_9\text{O}_2\text{Ag}$ . Calculated %: Ag 51.53.

#### CONCLUSIONS

1. For the first time butylisopropylacetylene has been synthesized and its physical constants determined.
2. The oxidation products of butylisopropylacetylene have been prepared, confirming its structure.

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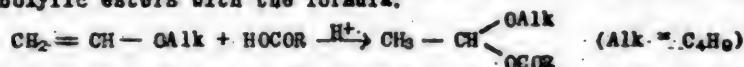
# ADDITION OF ALIPHATIC MONOCARBOXYLIC ACIDS TO VINYL ALKYL ETHERS.

## SYNTHESIS OF ALKOXYETHYLIDENECARBOXYLIC ESTERS

M. G. VORONOKOV

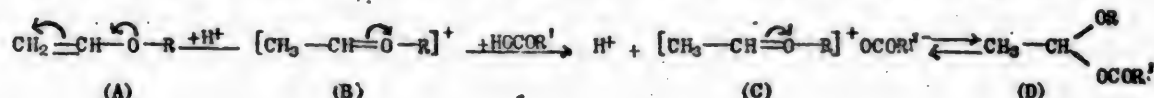
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Up to the present time, with the exception of a single patent [1], the addition reaction of organic acids and vinyl alkyl ethers has been totally ignored in the literature. Shostakovskiy and the author of the present paper thoroughly investigated the acidification of vinyl butyl ether [2]. In agreement with the patent specifications, it was demonstrated that the aliphatic monocarboxylic acids, which are hardly added to the olefins at all in the absence of a catalyst, are easily condensed with the input vinyl ether under mild temperature conditions. The reaction, which takes place autocatalytically, and is accompanied by a considerable exothermic effect, results in the formation, with a good yield, of butoxyethylidene carboxylic esters with the formula:



The reaction is extremely smooth in the presence of traces of phosphoric acid, which serves as a catalyst.

The mechanism of the acidification reaction of vinyl alkyl ethers seems to us to be as follows. The increased reactivity of the vinyl alkyl ethers in addition (and polymerization) reactions is due to the resonance of the carboxyl ion structure  $\text{CH}_2=\text{CH}=\text{O}^+-\text{R}$ . This structure originates because of the resonance between the unshared  $\pi$ -electrons of the oxygen atom and the electrons linked to this atom by a  $\pi$ -bond, which gives rise to a transfer of nucleophilic activity from the oxygen to the  $\beta$  carbon atom ( $\text{CH}_2=\text{CH}-\text{O}^+-\text{R}$ ). And since the middle carbon atom does not need to acquire a positive charge in this process, as the latter is transferred to the oxygen, which is able to hold this charge, the system  $\text{C}=\text{C}-\text{O}$  possesses a very much higher reactivity than the system  $\text{C}=\text{C}-\text{C}$ . Thus, the presence of protons (or of other electrophile agents) causes the activation of the double bond of the molecules of the vinyl alkyl ether at the expense of the addition of the proton to the  $\beta$  carbon atom:



The carboxylic cation (B) formed thereby, interacting with the molecular (or anionic) acid, forms the alkoxyethylidenecarboxy ester (D) via the carboxylic complex (C).

It was earlier noted [2] that under certain conditions (with fairly strong acids and at high temperature) the acidification reaction of vinyl alkyl ethers could occur with the formation of acetaldehyde and alkylcarboxylic ester. This latter course of the reaction may be explained by the fact that the intermediate carboxylic complex (C) decomposes like other tertiary oxonium compounds [3] as follows:



\* For convenience, the symbols used in the equations are those employed in electronic theory.



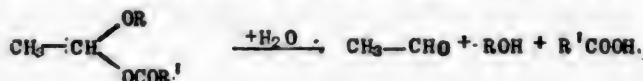
It should also be pointed out that in the acidification of vinyl alkyl ethers the corresponding ethylidene acetals are always formed as by-products. The mechanism of this reaction has been considered previously [2].

In the present paper it is demonstrated that, like vinyl butyl ether in the presence of traces of phosphoric acid, other vinyl alkyl ethers  $\text{CH}_2=\text{CH}-\text{OAlk}$  ( $\text{Alk}=\text{C}_2\text{H}_5, \text{C}_3\text{H}_7, \text{iso-C}_4\text{H}_9, \text{iso-C}_5\text{H}_{11}, \text{C}_7\text{H}_{15}$ ) also react smoothly with aliphatic monocarboxylic acids to form the corresponding alkoxy ethylidene carboxylic esters. In the case of formic acid the reaction occurs without a catalyst. The yields of alkoxy ethylidene carboxylic esters ranges from 75% to 95% of the theoretical and, apparently, increase with the rise in the molecular weight of the input ether or with a drop in the dissociation constant of the acid employed.

The alkoxy ethylidene carboxylic esters, like other compounds with alkoxy and carbo-alkoxy groups attached to a single carbon atom, are called alkyl acyl acylals by Hurd [4]. These relatively little-investigated compounds have been obtained up to the present time chiefly by the action of salts of organic acids upon  $\alpha$ -halogen ethers [4,5,6]. Ethoxy ethylidene acetate, which has been described only very superficially, was prepared by heating diethyl acetate with acetic anhydride [7]. The stable hemi-acetals (such as the chloral alcoholates) likewise form the corresponding alkoxy ethylidene carboxylic esters upon reaction with the acid chlorides [8].

The proposed method of synthesizing the alkoxy ethylidene carboxylic esters from the vinyl alkyl ethers is the most convenient and efficient, owing to its extreme simplicity, high yields, and the availability of its raw materials.

The alkoxy ethylidene carboxylic esters, like all the alkyl acyl acylals [9], are easily and rapidly hydrolyzed by dilute acids and alkalis, while some of them are even hydrolyzed by boiling with water, with the formation of acetaldehyde, alcohol, and acid:



This hydrolysis reaction of the alkoxy ethylidene carboxylic esters in an alkaline medium was employed by us for quantitative determinations.

#### EXPERIMENTAL

The input vinyl alkyl ethers were prepared either by the Favorsky-Shostakovsky method [10], or by splitting off alcohols from the corresponding ethylidene acetals by means of aniline sulfate or sodium bisulfate. The ethers obtained are carefully purified, being repeatedly washed for this purpose with an alkaline solution and then with water, after which they are desiccated over potash and distilled over fused KOH. The ethers are then treated with metallic sodium in the cold, and then distilled into a column to eliminate the latter. The vinyl alkyl ethers thus purified produce absolutely no change on the brilliant surface of sodium, while upon analysis by the method of hydrolytic oxime formation [11], they prove to be 99.8-99.9% pure. Their constants are listed in Table 1. The listed boiling points and densities are in good agreement with the data reported by Prilezhayeva and Shostakovsky [12], for pure vinyl alkyl ethers. The constant difference in the refractive indices for the D line (0.0013) are apparently due to an instrumental error in the refractometer employed by the authors cited.

The input acids were likewise subjected to purification (special care being taken with the removal of water).

\* The values of surface tension ( $\gamma^{20}$ ) and the refractive indices for the C and F lines for the vinyl alkyl ethers are given here for the first time. Likewise, vinyl n-heptyl ether is also described for the first time.

TABLE 1  
Physical Constants of Vinyl Alkyl Ethers

Ether	B. p. °C	n <sub>D</sub> <sup>20</sup>	d <sub>4</sub> <sup>20</sup>	n <sub>D</sub> <sup>25</sup>	d <sub>4</sub> <sup>25</sup>	n <sub>D</sub> <sup>30</sup>	d <sub>4</sub> <sup>30</sup>	MR <sub>D</sub>		γ <sub>20</sub> ± 0.10 STK cm <sup>2</sup>	P	
								Found	Calculated		Found	Calculated
CH <sub>2</sub> =CH-OC <sub>2</sub> H <sub>5</sub> . . . . .	36.38	789.8	0.7531	1.37396	1.37657	1.38280	22.00	21.85	19.00	199.8	199.2	
CH <sub>2</sub> =CH-OC <sub>3</sub> H <sub>7</sub> . . . . .	64.94	762.4	0.7674	1.38839	1.39084	1.39706	26.64	26.47	20.62	239.0	238.2	
CH <sub>2</sub> =CH-OC <sub>4</sub> H <sub>9</sub> . . . . .	93.98	766.5	0.7792	1.39910	1.40166	1.40787	31.26	31.08	21.95	278.2	278.2	
CH <sub>2</sub> =CH-OC <sub>5</sub> H <sub>11</sub> . . . . .	81.21	771.2	0.7683	1.39398	1.39656	1.40263	31.31	31.08	20.54	277.6	277.2	
CH <sub>2</sub> =CH-OC <sub>3</sub> H <sub>7</sub> -iso . . . . .	111.8	743.9	0.7826	1.40471	1.40721	1.41336	35.94	35.71	22.48	317.7	316.2	
CH <sub>2</sub> =CH-OC <sub>4</sub> H <sub>9</sub> -iso . . . . .	169.3-169.6	753.6	0.8021	1.41918	1.42200	1.42808	45.06	44.94	25.15	398.3	395.2	

\*By the Segden method

TABLE 2  
Alkoxy Ethylidene Carboxylic Esters CH<sub>3</sub>CH(OR)OCOR'

Ester	T. ANN. ± 0.2° C	n <sub>D</sub> <sup>20</sup>	d <sub>4</sub> <sup>20</sup>	n <sub>D</sub> <sup>25</sup>	MR <sub>D</sub>		XMR <sub>D</sub>	M		SWAGE %	ANAL. % R'COOH	
					HALENO	SHVCHAGHO		HALENO	SHVCHAGHO		HALENO	SHVCHAGHO
CH <sub>3</sub> CH(OC <sub>2</sub> H <sub>5</sub> )COOH* . . . .	113.8- 115.3	781.4	0.9511	1.3846	29.08	28.58	0.50	115.4 116.6	118.14	83.5	39.09 39.09	38.96
CH <sub>3</sub> CH(OC <sub>3</sub> H <sub>7</sub> )CCOCH <sub>3</sub> ** . .	129.7- 130.0	760.0	0.9460	1.39132 <sup>a</sup>	33.22	33.20	0.02	132.0 131.5	132.17	75.0	45.40 45.37	45.44
CH <sub>3</sub> CH(OC <sub>3</sub> H <sub>7</sub> )OCOC <sub>2</sub> H <sub>5</sub> . .	53.5	20	0.9376	1.3974	37.99	37.82	0.17	—	146.19	88.0	50.72 50.72	50.67
CH <sub>3</sub> CH(OC <sub>3</sub> H <sub>7</sub> )OCOC <sub>3</sub> H <sub>7</sub> . .	59.0- 59.5	15	0.9214	1.4043	42.55	42.44	0.11	163.3 161.9	160.21	86.0	54.88 54.85	55.00
CH <sub>3</sub> CH(OC <sub>3</sub> H <sub>7</sub> )OCOC <sub>4</sub> H <sub>9</sub> * . .	69.8- 70.4	13	0.9082	1.4039	47.21	47.06	0.15	170.4 171.3	174.23	84.5	58.62 58.53	58.62
CH <sub>3</sub> CH(OC <sub>3</sub> H <sub>7</sub> )COOH* . . . .	55.5	32.5	0.9300	1.3921	33.85	33.20	0.65	128.8 129.4	132.17	79.0	34.68 34.72	34.82
CH <sub>3</sub> CH(OC <sub>3</sub> H <sub>7</sub> )OCOCH <sub>3</sub> . . . .	55.0	20	0.9246	1.3980	38.16	37.82	0.34	150.1 149.3	146.19	84.0	41.00 41.10	41.10
CH <sub>3</sub> CH(OC <sub>3</sub> H <sub>7</sub> )OCOC <sub>2</sub> H <sub>5</sub> . .	63.1- 63.6	18	0.9186	1.4026	42.52	42.46	0.06	157.8 159.0	160.21	87.0	46.10 46.16	46.24
CH <sub>3</sub> CH(OC <sub>3</sub> H <sub>7</sub> )OCOC <sub>3</sub> H <sub>7</sub> . .	73.5- 73.9	15	0.9122	1.4067	46.99	47.06	-0.07	170.4 171.6	174.23	90.0	50.60 50.41	50.59
CH <sub>3</sub> CH(OC <sub>3</sub> H <sub>7</sub> )OCOC <sub>4</sub> H <sub>9</sub> * . .	76.6- 76.9	10	0.9083	1.4108	51.53	51.68	-0.15	184.2 185.9	188.26	95.4	54.16 54.09	54.25
CH <sub>3</sub> CH(OC <sub>4</sub> H <sub>9</sub> )OCOCH <sub>3</sub> . . . .	70.5	22	0.9198	1.4059	42.77	42.46	0.33	—	160.21	80.0	37.40 37.43	37.48
CH <sub>3</sub> CH(OC <sub>4</sub> H <sub>9</sub> )OCOC <sub>2</sub> H <sub>5</sub> . . .	71.8	12	0.9109	1.4081	47.20	47.08	0.14	174.2 173.8	174.23	88.0	42.56 42.58	42.53
CH <sub>3</sub> CH(OC <sub>4</sub> H <sub>9</sub> -H <sub>2</sub> O)OCOCH <sub>3</sub> .	88.0	66	0.8970	1.40033 <sup>b</sup>	43.33	42.46	0.87	159.5 160.1	160.21	82.5	37.42 37.40	37.48
CH <sub>3</sub> CH(OC <sub>4</sub> H <sub>9</sub> -H <sub>2</sub> O)OCOC <sub>2</sub> H <sub>5</sub> * .	96.2- 97.5	62	0.8918	1.3960	47.15	47.06	0.09	172.6 170.9	174.23	92.0	42.60 42.50	42.53
CH <sub>3</sub> CH(OC <sub>4</sub> H <sub>9</sub> -H <sub>2</sub> O)OCOCH <sub>3</sub> .	109.2- 110.0	79	0.8996	1.40617 <sup>c</sup>	47.59	47.06	0.53	170.0 171.7	174.22	90.0	34.33 34.36	34.47
CH <sub>3</sub> CH(OC <sub>5</sub> H <sub>11</sub> )OCOCH <sub>3</sub> * . . .	100.0- 102.0	11	0.9114	1.4275	57.05	56.30	0.75	197.2 198.8	202.29	92.0	29.50 29.44	29.69

\*Synthesized and described for the first time.

\*\*Literature data on ethoxy ethylidene acetate:

Blaisen [12], b.p. 125-130°C.

For data in the literature for the other known alkoxy ethylidene carboxylic esters (not marked with asterisks, C.F. Hurd, Green [3]).

<sup>a</sup> n<sub>D</sub><sup>20</sup> 1.38936; n<sub>D</sub><sup>25</sup> 1.39626; γ<sub>20</sub> 26.00. Found: P 315.5; Computed: P 314.0 by

Segden method

<sup>b</sup> n<sub>D</sub><sup>20</sup> 1.39841; n<sub>D</sub><sup>25</sup> 1.40526; γ<sub>20</sub> 24.83. Found: P 398.8; Computed: P 392.2.

<sup>c</sup> n<sub>D</sub><sup>20</sup> 1.40411; n<sub>D</sub><sup>25</sup> 1.41118.

The formic acid was dehydrated by a patented process [13], checked and modified by Pryanishnikov and Shakhova [14], frozen and distilled. The acetic acid was purified by freezing, followed by distillation. The propionic, butyric, and n-valeric acids were distilled just before they were introduced into the reaction.

The acidification reaction of the vinyl alkyl ethers was carried out in a three-necked round-bottomed flask, equipped with a stirring rod fitted with a mercury seal, a dropping funnel, a reflux condenser, a calcium chloride tube, and a thermometer.\*

Quantities of the corresponding acid, in which 2-3 drops of  $H_3PO_4$  ( $d = 1.7$ ) have been dissolved, are added to the initial ether. After 1-3 minutes have elapsed the temperature of the reaction mixture rises sharply. With vinyl ethyl and vinyl isopropyl ethers (especially when acidifying with formic acid) the reaction sets in instantaneously and is quite violent, so that external cooling is required. External cooling is also desirable in other cases, inasmuch as it slightly increases the yields of the alkoxy ethylidene carboxylic esters by reducing the formation of byproducts (dialkyl-acetylene, alkyl carboxylic ester, acetaldehyde, and alcohol). The reaction mixture is allowed to stand overnight, after which it is washed with a soda solution chilled to  $0^\circ C$ , desiccated with potash, and distilled in vacuo. The yields are 75-95% of theoretical. The alkoxy ethylidene carboxylic esters thus prepared are colorless liquids with a very pleasant fruity odor (with the exception of ethoxy ethylidene formate, which has a somewhat sharp odor) and a pleasant sweetish-sour taste. They are easily and rapidly hydrolyzed by dilute acids and alkalis, as well as by boiling with water, forming acetaldehyde and the corresponding alcohol and acid. The esters of the higher acids are harder to hydrolyze than the esters of the lower ones. The latter gradually decompose under the influence of moisture, even in storage, into acetaldehyde, alcohol, and acid, this phenomenon accounting for the increasingly sharp odor of the preparation as time passes. The physical constants of the alkoxy ethylidene carboxylic esters, their yields, and the analytical data obtained by the method of hydrolytic cleavage (described below) are given in Table 2. As may be seen from this table, all the alkoxy ethylidene carboxylic esters yield values for molecular refraction that differ somewhat from the theoretical values computed by the Lorentz formula, based on the Eisenlohr increments. Hurd and Green have already called attention to this fact [4]. It should be noted, however, that the molecular refraction found was higher than that computed theoretically in nearly all instances.

#### Quantitative Determination of Alkoxy Ethylidene Carboxylic Esters

The quantitative determination of the alkoxy ethylidene carboxylic esters is based upon the extremely easy and smoothly effected reaction of their hydrolytic cleavage. The determination is made as follows: a measured volume of 0.1 N aqueous solution of NaOH is added to a weighed portion of an alkoxy ethylidene carboxylic ester in a thick walled conical flask fitted with a ground-glass stopper; the contents are vigorously agitated until all the ester is dissolved, the flask being heated over a water bath. Then 1-2 drops of an alcoholic solution of phenolphthalein or thymolphthalein are added, and the contents of the flask titrated against 0.1 N HCl until the solution becomes colorless. The excess alkali is computed from the amount of acid used. By subtracting this excess from the quantity of NaOH solution used initially we obtain the amount of NaOH required to neutralize the acid formed from the alkoxy ethylidene carboxylic ester ( $V_B$ ). Baryta water may be employed instead of caustic soda.\*\* The amount of carboxylic acid in the ester is determined from the formula:

$$\% RCOOH = \frac{M_A}{10S} N_B \cdot V_B$$

where  $M_A$  = the molecular weight of the RCOOH acid;  $S$  = the weighed quantity of the ethylidene

\* For the vinyl alkyl ethers with fairly high boiling points the reaction can be performed in an ordinary flask, into which a thermometer is fitted for control purposes.

\*\* We established the titer of the alkali with pure ethoxy ethylidene acetate.

carboxylic ester;  $N_B$  = the normality of the alkaline solution employed; and  $V_B$  = the volume of alkali used to neutralize the carboxylic acid. As indicated in Table 2, the accuracy of the method is 0.1-0.2% (absolute). Alkoxy ethylidene carboxylic esters can also be determined by the method of hydrolytic oxidation worked out by the author [1].

#### CONCLUSIONS

The addition reaction of aliphatic monocarboxylic acids and vinyl alkyl ethers:  $\text{CH}_2=\text{CH}-\text{OAlk}(\text{Alk}=\text{C}_2\text{H}_5, \text{C}_3\text{H}_7, \text{C}_4\text{H}_9, \text{iso-C}_5\text{H}_{11}, \text{and } \text{C}_7\text{H}_{15})$  is investigated and the mechanism of the reaction is outlined.

Using the reaction of the acidification of vinyl alkyl ethers, which is a simple and convenient method of synthesizing alkoxy ethylidene carboxylic esters, we prepared a number (16) of these compounds with good yields (seven of them for the first time) and described them.

The method of quantitative determination of alkoxy ethylidene carboxylic esters is set forth.

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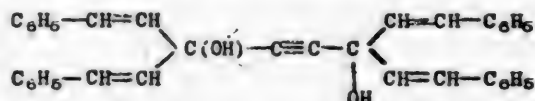


# THE SYNTHESIS OF ACETYLENIC $\gamma$ -GLYCOLS

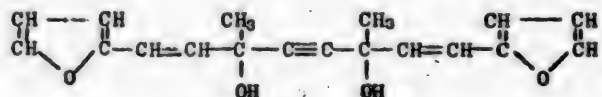
V. D. Yasnopolsky

As is well known, furfural in its chemical properties closely resembles the aromatic aldehydes, especially benzaldehyde; as a result, it may be employed in the synthesis of the acetylenic  $\gamma$ -glycols, as indicated by Yotsich [1]. This has already been demonstrated by the synthesis of difuryl-butinediol [2], which is an analog of diphenylbutinediol, synthesized for the first time by Dupont [3].

From the standpoint of the influence of radicals upon the properties of acetylenic  $\gamma$ -glycols when the phenyl radicals in the latter are replaced by furan groups, it would be of interest to synthesize new homologs of these glycols, which would contain ethylene groups in addition to the phenyl and furan radicals. In the present paper dibenzalacetone and furfuralacetone were employed, in the syntheses, yielding the following glycols: tetrastyril-butinediol

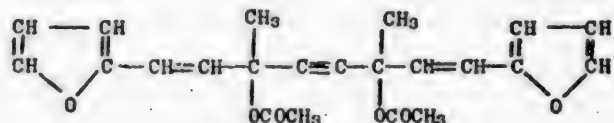


and 1,8-difuryl-3,6-dimethyl-octadiene-1,7-in-4-diol-3,6



Whereas the first glycol is a fairly stable crystalline substance, the second is an oily liquid, distillable in vacuum and tending toward polymerization under varying conditions.

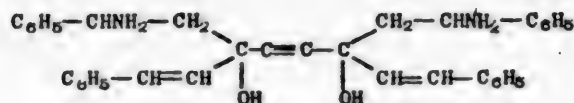
For the 1,8-difuryl-3,6-dimethyl-octadiene-1,7-in-4-diol-3,6 we obtained the acetic ether:



This ether proved to be a light yellow liquid, gradually darkening in color and possessing a characteristic odor.

Comparison of the properties of difuryl-butinediol and 1,8-difuryl-3,6-dimethyl-octadiene-1,7-in-4-diol-3,6 with those of glycols containing phenyl groups made it possible to isolate the characteristic properties imparted to these glycols by the furan groups. First of all, these glycols are oily substances with a specific gravity higher than one. Furthermore, these glycols possess the property of various polymerizing transformations, in varying degree.

As a derivative tetrastyril-butinediol, we synthesized an acetylenic  $\gamma$ -glycol with two amino groups: 3,6-distyryl-1,8-diphenyl-1,8-diamino-octine-4-diol-3,6.



This glycol was prepared as a light brown powder, which decomposed upon heating. Like other amines, this glycol yielded a picrate that was likewise a light-brown powder that decomposed upon heating. That is why it was found impossible to determine the melting points of these substances.

As for the synthesis of difuryl-butinediol, previously prepared [2], I think it is not superfluous to point out the following. When the glycol was synthesized repeatedly, it was found that, using the theoretical quantities of the input materials as a basis, some 50% of the furfural never entered into the reaction. To avoid the necessity of purifying the difuryl-butinediol later on, it was found advisable to use exactly 50% of the furfural for the synthesis that was theoretically required. To avoid resin formation the reaction mass must not be allowed to settle for more than 8 hours after the addition of furfural to the acetylene dimagnesium dibromide. To judge by the elementary composition, this would produce a completely pure glycol. This glycol oxidizes upon long exposure to air, turning into a powder that is insoluble in the usual organic solvents, resists the action of sulfuric and nitric acids, and does not fuse up to 250°C. Its elementary composition is: C - 61.49%; H - 3.61%.

#### EXPERIMENTAL

##### Preparation of 1,8-difuryl-3,6-dimethyl-octadiene-1,7-in-4-diol-3,6

Into an ether mixture of acetylene dimagnesium dibromide, prepared (according to Yotsich) from 24 g. of magnesium and 120 g. of ethyl bromide, subsequently saturated with acetylene, 110 g. of furfuralacetone in a benzene solution is introduced drop by drop. The initial furfuralacetone was synthesized by the method described by Gilman and Blatt [4], the condensation of furfural and acetone, and fused at 37-38°C. The reaction set in instantaneously, with the evolution of much heat. The reaction mixture was allowed to stand for three days, after which 300 ml. of water were gradually added to the solidified mass. At first no reaction occurred when this was done, since the whole mass was covered with a film of a resinous substance, so that the mass first had to be broken up with a spatula, after which the water was added. The reaction with the water was violent, liberating large quantities of heat. The cooled reaction products, which consisted of dark-brown solid and liquid phases, were separated by means of a Buchner funnel, the solid residue on the funnel filter being washed repeatedly with hot benzene. After separation from the aqueous layer the benzene extract was desiccated with calcium chloride; the benzene was then driven off over a water bath, its remaining traces being removed in vacuum. The end product was 98 g. of a brown oily liquid, which was subjected in turn to vacuum distillation, the following fractions being obtained:

- 1) 119-125°C (18 mm) . . . . 20 g.
- 2) 125-195°C (17 mm) . . . . 19 g.

A slight amount of decomposition then set in, the distillation being continued under the same vacuum until the onset of evident decomposition; this yielded an additional 16 g. of a dark-brown liquid. All three fractions were combined and subjected to another distillation in vacuum, yielding 27 g. of a fraction with a b.p. of 104-106°C (10 mm) as a light yellow, mobile, oily liquid with a slight characteristic odor, which, to judge from its analysis, was the sought-for glycol; its  $d_4^{25}$  was 1.0296.

0.0948 g. substance: 0.2516 g. CO<sub>2</sub>; 0.0555 g. H<sub>2</sub>O.  
 Found %: C 72.2; H 6.50  
 C<sub>22</sub>H<sub>24</sub>O<sub>4</sub>: Calculated %: C 72.4; H 6.04.

The liquid gradually grows darker upon standing exposed to light. Resinification

occurs instantaneously in sulfuric acid, while when heated with a 10% solution of KOH the liquid decomposes, liberating acetylene (a white precipitate is formed in an ammoniacal solution of silver oxide). The glycol polymerizes easily under the action of various substances. When it is agitated with ammonia for 12 hours, for instance, the glycol is converted into a thick dark-brown tar.

#### Preparation of 1,8-Difuryl-3,6-dimethyl-octadiene-1,7-in-4-diol-3,6 Acetate

10 g. of the glycol mixed with 40 g. of acetic anhydride and 5 g. of sodium acetate are heated over a water bath for one hour, the mixture then being poured out over ice. The oil obtained was separated from the remaining liquid and washed several times with water, after which 5.5 g. of the oil was subjected to vacuum distillation. The following fractions were obtained:

- 1) 99-101°C (10 mm) . . . . 1.5 g.
- 2) 101-115°C (10 mm) . . . . 1 g.

The first fraction, straw-yellow in color, which darkened upon exposure to light, and slightly oily to the touch, had a characteristic, somewhat spicy, vegetation-like odor, and to judge by the elementary analysis, it was the acetate sought after; its  $d_4^{25}$  was 0.8771.

0.1087 g. substance: 0.2756 g. CO<sub>2</sub>; 0.0582 g. H<sub>2</sub>O.  
 Found %: C 69.14; H 6.1.  
 C<sub>22</sub>H<sub>22</sub>O<sub>6</sub>. Calculated %: C 69.11; H 5.75.

#### Preparation of Tetrasteryl-butinediol

Into an ethereal mixture of acetylene dimagnesium dibromide, prepared (according to Yotsich) from 24 g. of magnesium and 120 g. of ethyl bromide subsequently saturated with acetylene, there was introduced drop by drop a benzene solution of 80 g. of dibenzalacetone, the whole being chilled and constantly stirred, after which the reaction mixture was allowed to stand for three days. The initial dibenzalacetone was synthesized by the method described by Blatt [5], the condensation of benzaldehyde and acetone, and melted at 104-108°C. After standing, the liquid phase of the reaction mixture was separated from the solid phase; the solid residue on the filter funnel was washed with hot benzene, and after the benzene extract had been freed of water and deacidified over calcium chloride, the benzene was driven off, first over a water bath and then in vacuum. As a result we obtained 42 g. of a transparent resinlike mass, which fused easily when the flask was plunged into hot water. By vacuum distillation 12 g. of a fraction was obtained with a b.p. of 134-156°C (15 mm), which crystallized at once. The crystalline mass was washed several times with cold alcohol. The powdery substance obtained had a pale yellow color and fused at 74-77°C. After two recrystallizations from alcohol we obtained white flaky crystals with a m.p. of 79-81°C, which dissolved in concentrated sulfuric acid, coloring the acid a lemon yellow, and appeared to be the sought-for glycol, according to the elementary analysis.

0.0546 g. substance: 0.1750 g. CO<sub>2</sub>; 0.354 g. H<sub>2</sub>O.  
 Found %: C 87.41; H 7.2.  
 C<sub>36</sub>H<sub>36</sub>O<sub>2</sub>. Calculated %: C 87.45; H 6.9.

#### Preparation of 3,6-difuryl-1,8-diphenyl-1,3-diamino-octane-4-diol-3,6.

The ketone 1,5-diphenyl-1-amino-pentene-4-one-3 was prepared by the action of ammonia on dibenzalacetone. Gaseous ammonia was passed through a saturated alcoholic solution of dibenzalacetone for 8 hours. The thick oil settling out was freed from alcohol; after standing exposed to air it hardened into a light-brown solid mass, which was then pulverized, with a m.p. of 92-95°C (decomposing). Nitrogen determination (by the Kjeldahl method) indicated that one molecule of ammonia had been added in the process.

0.0313 g. substance: 1.3 ml 0.1 N. H<sub>2</sub>SO<sub>4</sub>  
 Found %: N 6.1.  
 C<sub>27</sub>H<sub>27</sub>ON. Calculated %: N 5.57.

In a benzene solution the substance bleached solutions of KMnO<sub>4</sub> and bromine water.

The glycol was synthesized as follows: A benzene solution of 10 g. of aminoketone was gradually added to an ether solution of acetylene dimagnesium dihydride, prepared from 60 g. of ethyl bromide and 12 g. of magnesium through which acetylene had been allowed to pass. The mixture was left to stand for 24 hours. A solution of ammonium sulfate was then allowed to drop into the reaction mass until all reaction ceased. After being allowed to stand for some time, the benzene layer was separated from the other reaction products and the benzene driven off over a water bath. The residue obtained was 8.5 g. of a transparent red substance smelling of pine. This substance was subjected to vacuum distillation (10 mm); up to 90°C there distilled over a few drops that instantly crystallized in needles with a m.p. of 43-45°C. The substance within the flask grew considerably darker, and the distillation was broken off. The residue in the flask hardened into a solid mass, which turned into a light-brown powder upon pulverization. When the substance was crystallized out of alcohol it separated in powder form. M.p. about 150°C.

0.0970 g. substance: 3.74 ml. 0.1 N.  $H_2SO_4$ .  
 0.2345 g. substance: 8.83 ml. 0.1 N.  $H_2SO_4$ .  
 Found %: N 5.30; 5.24  
 $C_{26}H_{36}N_2$ . Calculated %: N 5.30.

When heated with a 10% solution of NaOH, the glycol decomposed, liberating acetylene (a precipitate was obtained with an ammoniacal solution of silver oxide).

The benzene solution of the glycol did not give an alkaline reaction with phenolphthalein. When a hot alcoholic solution of picric acid was added to a hot alcoholic solution of the glycol, allowing two molecules of acid per molecule of glycol, a precipitate was thrown down at once. The liquid was decanted 24 hours later, and the chilled precipitate was washed with alcohol and then with water until all the picric acid had been removed. The precipitate was ground to a powder, which fused at about 185°C. The Kjeldahl determination of nitrogen indicated that the substance was the addition product of one molecule of picric acid and one molecule of the glycol.

0.0330 g. substance: 2.06 ml. 0.1 N.  $H_2SO_4$   
 0.0480 g. substance: 2.98 ml. 0.1 N.  $H_2SO_4$   
 Found %: N 8.78; 8.70.  
 $C_{36}H_{36}O_2N_2 \cdot C_6H_3O_7N_3$ . Calculated %: N 9.24.

#### CONCLUSIONS

1. Tetrastyril-butinediol and 1,8-difuryl-3,6-dimethyl-octadiene-1,7-in-4-diol-3,6 were prepared for the first time and their properties described.
2. An acetylenic  $\gamma$ -glycol with two amino groups -- 3,6-distyril-1,8-diphenyl-1,8-diamino-octane-4-diol-3,6 -- was prepared.

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# ISOMERIZATION OF UNSATURATED HYDROCARBONS UPON CONTACT WITH METAL OXIDES

## VIII. ISOMERIZATION OF HEXINE-1 OVER CHROMIC OXIDE ON ALUMINA

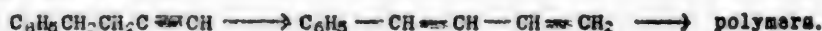
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In one of our communications [1] we described the contact isomerization of an aromatic hydrocarbon with a triple bond in a side chain -- 4-phenyl-butine-1. It was shown that this  $\alpha$ -acetylenic hydrocarbon undergoes extensive isomerization at 250°C when in contact with chromic oxide, the triple bond being shifted from the first to the third carbon atom of the side chain, i.e.; with the formation of 4-phenyl-butine-3.

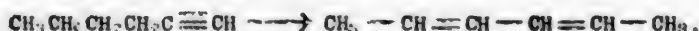


In some experiments the yield of 4-phenyl-butine-3 was no more than 25-40% of the hydrocarbon used; the formation of a considerable quantity of polymers was observed. This circumstance suggested that one of the products of the isomerization of 4-phenyl-butine-1 was 1-phenyl-butadiene-1,3, which, to judge by the data in the literature [2], polymerizes easily upon heating:

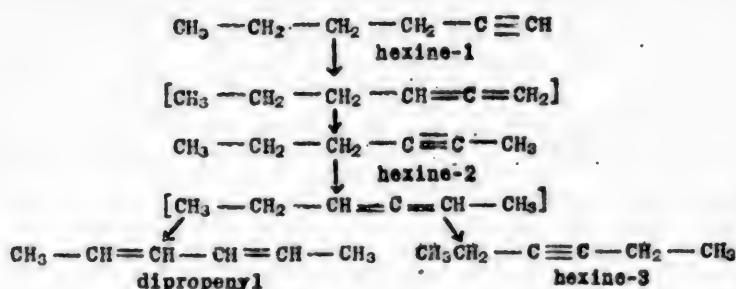


In the present paper the contact isomerization of an  $\alpha$ -acetylenic hydrocarbon with an open chain of carbon atoms -- hexine-1 -- is investigated. Chromic acid deposited on alumina was used as the contact agent; this is a composite contact that is just as active, but much more durable [3] than pure chromic oxide.

When hexine-1 was passed over chromic oxide on alumina at 250°C we obtained (with a yield of 60% of the input hydrocarbon) a condensate that contained none of the initial  $\alpha$ -acetylenic hydrocarbon. The presence in the condensate of a hydrocarbon with a conjugate system of double bonds -- dipropenyl -- was proved by the reaction with maleic anhydride. To judge by the refractive index of the condensate (after driving off the polymeric forms produced) it contained 54% of dipropenyl:



After the dipropenyl had been removed by heating with maleic anhydride, the remainder of the condensate consisted (as its constants indicated) of a mixture of hexine-2 and hexine-3. The process of isomerization was accompanied by the formation of a considerable quantity of polymers with higher boiling points. Inasmuch as dipropenyl does not polymerize in the presence of chromic oxide on alumina [4], we were led to assume that the allene hydrocarbons formed as intermediate products are subjected to partial polymerization. Thus, in the presence of chromic oxide on alumina the  $\alpha$ -acetylenic straight-chain hydrocarbons undergo thoroughgoing isomerization, the triple bond being converted into two double bonds constituting a symmetrical conjugated system, as well as being shifted within the molecule.



The process of isomerizing hexine-1 to dipropenyl must take place in a large number of intermediate stages (see above); this conversion of the  $\alpha$ -acetylenic hydrocarbon into an isomeric symmetrical diene hydrocarbon with a conjugate system of double bonds ("symmetrization" of the molecule) takes place when hexine-1 passes over the catalyst only once.\*

#### EXPERIMENTAL

Hexine-1 was prepared from 1,2-dibromohexane, obtained by the bromination of hexane-1, which in turn was synthesized by the action of allyl chloride on propyl magnesium iodide. The splitting off of two molecules of hydrogen bromide from the 1,2-dibromohexane (b.p. 61-62°C at 4 mm;  $n_D^{20}$  1.5010) was effected with sodium amide (by Bourguet's method [5]) in a kerosene\*\* solution at 160-170°C. After heating for 8 hours the reaction mixture was decomposed in water, the kerosene layer was removed, and the reaction product -- hexine-1 -- was driven off by steam. After redistillation with a tall Vigreux dephlegmator (height of the dephlegmating section - 0.5 m), the hexine-1, desiccated over calcium chloride, possessed the following constants (yield was 76% of theoretical):

B.p. 70.5-71°C (750 mm);  $n_D^{20}$  1.3993;  $d_4^{20}$  0.7149;  $M_D$  27.78.

$C_6H_{10}$ .  $F$  calculated:  $M_D$  27.90.

Literature data: Bourguet [5] -- b.p. 71-72°C,  $n_D^{20}$  1.4020,  $d_4^{17}$  0.721. Risseghem [6] -- b.p. 71.35-71.4°C (760 mm),  $d_4^{20}$  0.7193; Campbell and Eby [7] -- b.p. 71.4°C,  $n_D^{20}$  1.3990,  $d_4^{20}$  0.7156.

The hexine-1 was passed over chromic oxide on alumina\*\*\* (inside diameter of the tube - 17 mm; length of the catalyst layer - 65 cm) in a weak current of nitrogen at 250°C and at a rate of 0.12-0.15 ml/min. The activity of the catalyst was checked by passing an easily isomerized hydrocarbon -- allylbenzene -- over it. The yield of condensate was 60% by weight of the hexine-1 employed; 20.5 g. of condensate was obtained from 30 g. of the hydrocarbon. When the catalyst was subsequently activated by heating it to 450°C in a stream of oxygen, another 6 g. of thick oil was obtained.

The condensate yielded no precipitate (nor did it even grow turbid) when acted upon by an alcoholic solution of silver nitrate; hence it contained no traces of the initial hexine-1. Upon distillation of the condensate (20.5 g), a fraction with a b.p. 78-82°C (750 mm),  $n_D^{20}$  1.4333 (16 g), i.e. 53% of the initial hexine-1. The boiling point (78-82°C) of this fraction indicated that it was a mixture of hexine-2 and hexine-3 -- the two possible products of the isomerization of hexine-1. However, its refractive index (1.4333) proved to be much higher than that for these two hydrocarbons (cf. table). This led us to assume that

\* Slobodin [8] observed the conversion of butene-1 into methylallene and to a much lesser degree into divinyl upon contact with fluoridin at 275°C. Hurd and Christ [10], in studying the pyrolysis of hexene-1 at 500 and 600°C, separated hexadiene-1,2, propylallene, and traces of hexene-2 from the liquid reaction products. There were no hydrocarbons with a conjugate system of double bonds in the condensate.

\*\*The kerosene (190-240°C fraction) was first treated with sulfuric acid, washed until its reaction was neutral, desiccated with calcium chloride, and distilled over metallic sodium.

\*\*\*The preparation of the chromic oxide on alumina has been described in a previous communication.

the isomerization product contained dipropenyl (hexadiene-2,4), a hydrocarbon with a conjugate system of double bonds (b.p. 80.5-82°C,  $n_D^{20}$  1.4512 [4]), that is an isomer of the hexines. To test this supposition part of the product of isomerization was condensed with maleic anhydride in a benzene solution [5]. After the benzene had been driven off (in vacuum), the solid residue treated with hot water to remove the unreacted maleic anhydride, and the reaction product recrystallized from ligroin, we obtained crystals with a m.p. of 93-94°C. A test of combined fusion with an adductive prepared from pure dipropenyl and maleic anhydride and possessing a m.p. of 93.5-94.5°C produced no depression.

Literature data for this adductive (n-dimethyl-tetrahydro-o-phthalic anhydride): Diels and Alder [6] -- m.p. 95-96°C.

Hydrocarbons	B.p.	$n_D^{20}$	$d_4^{20}$	Literature data
Hexine-1 . . . . .	71.4°C	1.3990	0.7156	[7]
Hexine-2 . . . . .	84-85	1.4135	0.740	[5]
Hexine-3 . . . . .	81	1.4115	-	[7]
Product of isomerizing hexine-1 after removing dipropenyl (81-82°C fraction) . . .	81-82	1.4167	0.7315	

Thus it was established beyond doubt that the contact of hexine-1 with chromic oxide on alumina effects its isomerization to dipropenyl. The refractive index of the isomerization product indicated that the percentage of dipropenyl in the product was 54%. But as the isomerization product obtained (78-82°C fraction) had a lower refractive index than dipropenyl, we were justified in assuming that it contained, in addition to the dipropenyl, other hydrocarbons that were isomers of hexine-1. To remove these latter from the dipropenyl, part of the condensate (12 g.) was heated over a water bath with maleic anhydride (18 g.) without any solvent for eight hours. The products of the isomerization of hexine-1 that did not enter into the reaction were extracted with ether. After the ether had been driven off, the residue (3 g.) was distilled (with a Vigret dephlegmator) at 81-82°C (744 mm); its constants (after redistillation) were close to the constants of hexine-2 and hexine-3 (cf. table).

#### Analysis of the 81-82°C fraction

4.882 mg. substance: 15.706 mg. CO<sub>2</sub>; 5.350 mg. H<sub>2</sub>O.  
 5.620 mg. substance: 18.060 mg. CO<sub>2</sub>; 6.170 mg. H<sub>2</sub>O.  
 Found %: C 87.67, 87.69; H 12.26, 12.28.  
 C<sub>6</sub>H<sub>10</sub> Calculated %: C 87.72; H 12.28.

#### CONCLUSIONS

1. The contact isomerization of an  $\alpha$ -acetylenic hydrocarbon over a composite catalyst has been investigated.
2. It has been found that an  $\alpha$ -acetylenic hydrocarbon with a normal carbon chain (hexine-1) completely undergoes thorough isomerization in a single pass over chromic oxide on alumina at 250°C, the triple bond being converted into two double bonds constituting a symmetrical conjugated system, as well as being shifted within the molecule.
3. Thus it has been found that chromic oxide on alumina possesses isomerizing properties not only for diene hydrocarbons with an isolated system of double bonds and for aromatic hydrocarbons with an unsaturated side chain, but also for  $\alpha$ -acetylenic hydrocarbons with an open carbon chain.

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## THE INTERACTION OF N-Cl AMINES AND AMINES

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F. Selivanov [1], while investigating the properties of N-Cl amines, came to the conclusion that these compounds, which enter into all the reactions characteristic of hypochlorous acid, should be considered as amides of hypochlorous acid. Using the chloroamines, Selivanov oxidized primary and secondary alcohols, as well as sulfurous and arsenious acid.

The oxidation of fats by the chloroamines may serve as an example of their oxidizing action; another is the oxidation of the derivatives of toluene and other substances, yielding acids and aldehydes [2]. The well known bleaching action of the chloroamines is likewise due to their oxidizing properties.

Like hypochlorous acid, the chloroamines behave like typical chlorinating agents. Selivanov and, later, Likhoshkerstov [3] employed chloroamines for chlorinating phenols and amines; Godohed and Pastureau [4] chlorinated unsaturated compounds by means of urea chloride; and so forth.

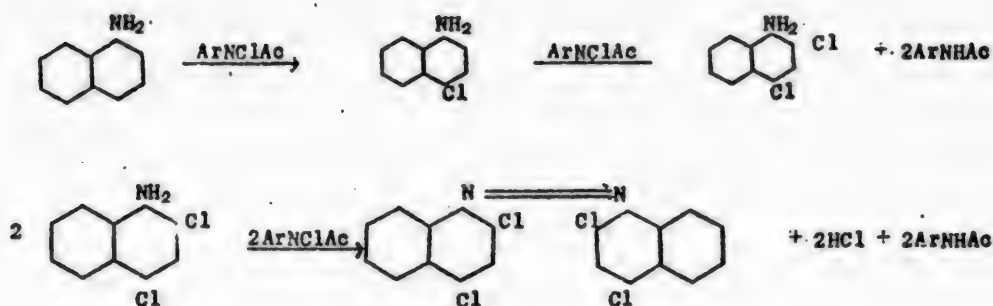
The object of the present study is the interaction of chloroamines with various amines for which data are available in the literature. Letting acetochloramide and chlorosuccinimide act on the primary and secondary aliphatic amines, Selivanov obtained N-chlorine derivatives of the aliphatic amines. The N-Cl reactions of acetanilide, phthalimide, and succinimide with secondary amines were subsequently investigated by Vassiliaden [5], who reported different results. In his opinion this case involves condensation with the substituted hydrazo compounds formed and the separation of hydrogen chloride according to the following equation:



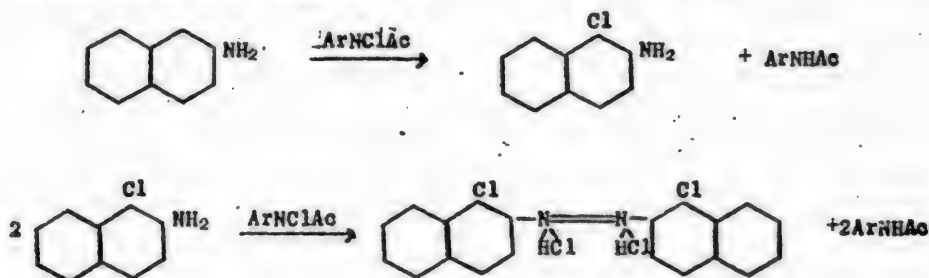
Chattaway and Orton [6] point out that when aniline is acted upon by N-Cl-acetanilide, chloranilines are formed in the ring, and that the fully chlorine-substituted trichloroanilines thus produced can be converted into hexachlorazobenzene by the action of an excess of chloroamine.

The subjects of our researches were the N-Cl-acyl anilines and toluidines, as well as various amines: aromatic, aliphatic, and aliphatic-aromatic.

Our experiments indicated that when the chloroamines act upon aromatic amines in an anhydrous organic medium, the benzene ring containing the amino group is first chlorinated, while when the chloroamine is present in excess, the amine chlorinated in the ring is oxidized to an azo compound in the case of primary amines. Thus,  $\alpha$ -naphthylamine with one molecule of a chloroamine yields n-chloronaphthylamine, with some of the o-isomer; with two molecules of the chloroamine it yields 2,4-dichloro- $\alpha$ -naphthylamine. But the consumption of the active chlorine is not confined to these two instances alone -- a third molecule of the chloroamine enters into the reaction, oxidizing the dichloronaphthylamine to its azo derivative.

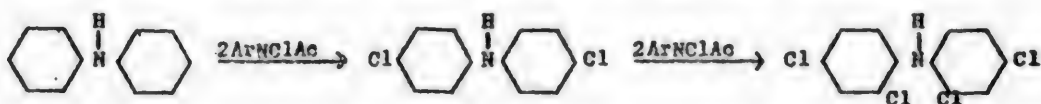


When  $\beta$ -naphthylamine is treated in the same manner, we obtain the dichloride of the azo derivative of monochloro- $\beta$ -naphthylamine.



In the latter case the formation may be explained as due to the high basicity of monoazonaphthol compared to the azo compounds prepared from dichloronaphthylamine, the basicity of which is lowered by the second chlorine atom.

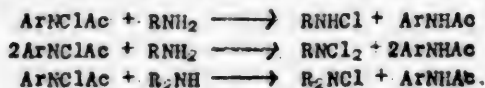
Added to diphenylamine, the chloramines yield di- and tetra- substitutions.



When it is borne in mind that the medium in which the experiments were carried out was anhydrous and thus did not facilitate any hydrolysis, it would be quite logical to explain the chlorination mechanism of the reactions as a double exchange (between the chlorine and hydrogen atoms attached to the nitrogen) with a subsequent shift of the chlorine within the amine ring, as was done by Chattaway and Orten for the chlorination of aniline. But this conclusion is refuted by the reaction with dimethylaniline, which takes place analogously to the one outlined above. Though, by analogy with the other tertiary amines (*vide infra*) we should expect the splitting off of one methyl group and the formation of a chlorine-substituted monomethylaniline as a result of the double exchange and the intramolecular regrouping, what we did obtain were high yields of mono-, di-, and trichloro-dimethylanilines. Evidently, the chlorination of dimethylaniline occurs in this instance directly as a simple exchange between the chlorine atoms of the chloro-amine and the ring hydrogen of the amine.

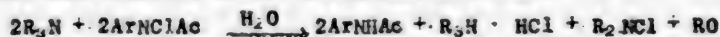


The chloroamines react with the primary and secondary aliphatic amines in a decomposition exchange, as Selivanov had already demonstrated:



In the reaction with tertiary amines, the formation of neither hydrazo compounds nor the hydrochlorides of the amine was found to occur, contrary to the observations of Vassiliades [5] under analogous conditions (an excess of the amine).

The reaction of chloroamines with tertiary aliphatic and aliphatic-aromatic amines, in which the nitrogen is bound to the aliphatic chain and not to the aromatic ring, is accompanied by the splitting off of a single alkyl group from the amines, its oxidation to an aldehyde, and the chlorination of the dialkylamine formed:



(where R - aliphatic radical, and RO - its corresponding aldehyde).

This course of the reaction may be explained as due, on the one hand, to the strong tendency of tertiary amines to form salts, and on the other, to the tendency of tertiary amines toward oxidizing decomposition.

The action of the chloroamines in this case is analogous to the action of hypochlorous acid on amines. Willstätter and Iglauer [6], for instance, observed a similar splitting-off reaction with the formation of tropidine perchlorate. Meisenheimer [7] allowed hypochlorous acid to act upon trimethyl amine and obtained the hydrochlorides of the dimethyl- and trimethyl amines as well as the aldehyde.

When the chloroamines react with amines, they themselves are fundamentally changed -- into acylanilines and toluidines, which, under the conditions prevailing in our experiments, precipitate out with quantitative yields. In this process no chlorination (intra-molecular regrouping) takes place within the molecule of the chloroamine.

#### EXPERIMENTAL

The reaction of the chloroamines with amines was effected in an organic solvent, principally in benzene solutions, at room temperature. For the most part, the raw materials employed were commercial amines and chloroamines, synthesized in our laboratory, carefully purified, and corresponding with the pure preparations described in the literature (benzoylated toluidines, etc.) insofar as boiling and melting points were concerned.

##### Action of Chloroamines Upon Aromatic Amines.

When chloroamines are mixed with primary and secondary amines in a benzene solution, the reaction is violent, with the evolution of heat, and is completed within 15-20 minutes. In this reaction the base of the chloroamine is always quantitatively regenerated in the form of a crystalline precipitate that is only slightly soluble in benzene or gasoline. By way of example let us consider the reaction of the chloroamines with  $\alpha$ - and  $\beta$ -naphthylamines and diphenyl amines not previously described in the literature. When equimolecular quantities of the chloroamine and  $\beta$ -naphthylamine are dissolved in a benzene solution, the solution turns brown, heats up, after which the base of the original chloroamine precipitates out. From the solution a crystalline product is obtained, taking the form of white needles with a b.p. of 57-58°C after recrystallization and corresponding to the 1-chloronaphthylamine-2 known in the literature:

0.2113 g. substance: 0.1700 g. AgCl.  
 Found %: Cl 19.91.  
 C<sub>10</sub>H<sub>8</sub>ClNH<sub>2</sub>. Calculated %: Cl 19.97.

The yield of the monochloroamine is 95-96% of theoretical. The reaction follows an

analogous course when the chloroamine is present in excess, but then the precipitate contains, in addition to the base of the chloroamine (I), another substance in the form of a fine yellow powder (II), which is insoluble in hot benzene, which made it possible to separate it. The quantity of (I) corresponds to the quantity of chloroamine employed in the reaction. The yellow compound (II), purified by exhaustive extractions with hot benzene, has no sharply marked melting point. It softens and grows darker above 150°C; it dissolves in alcohol and in glacial acetic acid, turning an intensive red, but is only slightly soluble in other solvents. When allowed to stand exposed to the air, the color of the surface layer changes rapidly, turning a darker red; upon boiling with water or upon alkalization, hydrogen chloride is set free, and all the powder turns dark red (III).

Substance (III) differs from the salt in that it is easily soluble in benzene, ether, chloroform, and acetone, but is very hard to dissolve in petroleum ether and ligroin; it does not crystallize and fuses somewhere in the neighborhood of 120°C; while with hydrogen chloride it yields the initial salt and bleaches a hydrochloric acid solution of  $\text{SnCl}_2$ .

From the mother liquor (the filtrates of I and II) we were able to separate a dark red product (IV), with a m.p. of 108-110°C and 17.9% of chlorine (by Carius's method). When (IV) was fused with the compound obtained from the yellow salt by the splitting action of  $\text{HCl}$ , no depression was observed. (IV) is reduced by stannous chloride, with the formation of a colorless product that turns red upon exposure to air and apparently is identical with the base (III). On the whole and allowing for the salt formed, the yield of the red base approaches the theoretical value.

#### Analysis of the Yellow Salt (II)

0.1243 g. substance: 0.2600 g.  $\text{CO}_2$ ; 0.0384 g.  $\text{H}_2\text{O}$ .  
 0.2012 g. substance: 0.4223 g.  $\text{CO}_2$ ; 0.0831 g.  $\text{H}_2\text{O}$ .  
 0.3058 g. substance: 16.20 ml.  $\text{N}_2$  (14°C, 750 mm).  
 0.3838 g. substance: 20.33 ml.  $\text{N}_2$  (14°C, 750 mm).

#### Chlorine, by Carius' Method

0.2114 g. substance: 0.2717 g.  $\text{AgCl}$ .  
 0.2000 g. substance: 0.25430 g.  $\text{AgCl}$ .

#### Chlorine split off, by Volhard's Method

0.2210 g. substance: 9.5 ml. 0.1 N  $\text{AgNO}_3$ .  
 0.2175 g. substance: 9.4 ml. 0.1 N  $\text{AgNO}_3$ .

Found %: C 57.04, 57.25; H 3.42, 3.46; N 6.11, 6.15;  
 Total Cl: 31.73, 31.48; Precipitated Cl 15.3, 15.3.

$\text{C}_{20}\text{H}_{12}\text{N}_2\text{Cl}_2 \cdot 2\text{HCl}$ . Calculated %: C 56.63; H 3.33; N 6.60; Total Cl 33.48;  
 Precipitated Cl 16.72.

Note: The drop in the percentage of total chlorine is explainable by the partial decomposition of the azochloronaphtholdichloride.

#### Analysis of the Red Base (III)

For analysis the base was precipitated by ammonia from an alcoholic solution of the yellow salt as a brick red powder, which was then washed and dried. M.p. 120°C.

0.2035 g. substance: 0.5109 g.  $\text{CO}_2$ ; 0.0655 g.  $\text{H}_2\text{O}$ .  
 0.2320 g. substance: 0.5704 g.  $\text{CO}_2$ ; 0.0751 g.  $\text{H}_2\text{O}$ .  
 0.2098 g. substance: 0.1889 g.  $\text{AgCl}$ .  
 0.2421 g. substance: 0.1884 g.  $\text{AgCl}$ .  
 0.1812 g. substance: 9.68 ml.  $\text{N}_2$  (16°C, 756 mm).  
 0.2000 g. substance: 13.4 ml.  $\text{N}_2$  (19°C, 742 mm).

Found %: C 68.46, 68.61; H 3.66, 3.63; N 7.00, 7.03;  
 Cl 19.30, 19.25.

$\text{C}_{20}\text{H}_{12}\text{Cl}_2\text{N}_2$ . Calculated %: C 68.38; H 3.44; N 7.97; Cl 20.19.

If a solution of stannous chloride in hydrochloric acid, with a sp. gr. of 1.19 (40 g. of stannous chloride in 100 ml. of acid, after Witt), is added to a red-colored solution of this substance (III) in glacial acetic acid or to an alcoholic solution, bleaching sets in at once; when the mixture is diluted with water only a slightly colored precipitate (V) is thrown down. The reduction product, carefully washed and dried, fuses at 138-140°C in a sealed capillary tube, but begins to fuse at the surface at 120°C in an open capillary; upon exposure to air it quickly turns red, being converted into the initial substance (III).

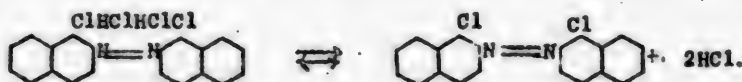


### Analysis of the Reduction Product (V)

0.2464 g. substance: 0.6204 g.  $\text{CO}_2$ : 0.0983 g.  $\text{H}_2\text{O}$ .  
 0.1134 g. substance: 0.2856 g.  $\text{CO}_2$ : 0.0461 g.  $\text{H}_2\text{O}$ .  
 0.2035 g. substance: 0.1806 g.  $\text{AgCl}$ : 0.1916 g. substance: 0.1508 g.  $\text{AgCl}$ .  
 0.1788 g. substance: 10.94 ml.  $\text{H}_2$  (16°C, 750 mm).  
 0.1665 g. substance: 10.14 ml.  $\text{H}_2$  (17°C, 748.6 mm).  
 Found %: C 68.67, 68.62; H 4.47, 4.52; Cl 19.50, 19.44; N 7.00, 6.94.  
 $\text{C}_{20}\text{H}_{11}\text{N}_2\text{Cl}_2$ . Calculated %: C 68.00; H 4.00; Cl 20.07; N 7.93.

This reduction product is easily oxidized to the initial substance, and its elementary composition enables us to conclude that it is a nitrogen derivative of chloronaphthylamine.

All this leads us to assume that the yellow precipitate is the hydrochloride of the nitrogen derivative of the chloronaphthylamine, which easily loses hydrogen chloride, turning into a base:



When chloroamines are reacted with  $\alpha$ -naphthylamines, a pinkish crystalline product separates out in the shape of needles with a m.p. of 97°C, containing a free primary amino group (red precipitate obtained by diazotization and subsequent combination with  $\beta$ -naphthol). Its melting point and its properties indicated that this substance was identical with *n*-chloro- $\alpha$ -naphthylamine

0.1988 g. substance: 0.1594 g.  $\text{AgCl}$ .  
 0.2366 g. substance: 0.1858 g.  $\text{AgCl}$ .  
 Found %: Cl 19.80; 19.88.  
 $\text{C}_{10}\text{H}_8\text{ClNH}_2$ . Calculated % Cl 19.97.

At first the chloronaphthylamine was purified by being driven off with steam, but this yielded small outputs of the substance. Most convenient was a method of separating the products via their salts. Concentrated hydrochloric acid was added to the mother liquor, precipitating the chloronaphthylamine hydrochloride, which is of a pale violet color. After careful washing with hot benzene, it was found to melt (soften) at about 195°C, and to dissolve in hot water and alcohol. A base -- *n*-chloronaphthylamine, with some of the ortho isomer -- is separated out under the action of ammonia and soda. The products yielded by the reaction were 85-97% of theoretical.

With an excess of the chloroamine (2 molecules) the chlorination of the naphthylamine molecule goes further, forming dichloronaphthylamine, which was quantitatively separated via the salt by means of hydrogen chloride. The salt has a m.p. of 186°C, thus corresponding, according to the data in the literature, to 2,4-dichloronaphthylamine. It is neutralized by sodium bicarbonate, a base with a m.p. of 80°C separating out, indicating a strongly marked reaction with the free amino group:

0.2000 g. substance: 0.2684 g.  $\text{AgCl}$ .  
 0.2000 g. substance: 0.2692 g.  $\text{AgCl}$ .  
 Found %: Cl 33.21, 33.35.  
 $\text{C}_{10}\text{H}_6\text{Cl}_2\text{NH}_2$ . Calculated %: Cl 33.44.

To judge from its melting point, chlorine content, and properties, this substance corresponds to 2,4-dichloro- $\alpha$ -naphthylamine.

When three molecules of the chloroamine are allowed to act upon a molecule of the  $\alpha$ -naphthylamine, the reaction solution turns an intense red and hydrogen chloride is liberated. The solution yielded a dark-red, almost black, tarry, uncrystallizable product that was soluble in alcohol, coloring the latter deeply. After removal of the solvent and prolonged drying in a vacuum exsiccator, it turned powdery with a m.p. of about 80°C and a chlorine content of 30.9%. When a hydrochloric acid solution of stannous chloride was added to an alcoholic

solution of this substance, the latter grew lighter. From an aqueous solution a precipitate settles out, which at once begins to darken upon exposure to air, turning into the initial product. No further investigation of these substances was undertaken, as they could not be obtained in the pure state. The data obtained enable us, however, to assume that here we have a case of the formation of the azo compound of dichloro- $\alpha$ -naphthylamine, which upon reduction is converted into the corresponding hydrazo compound and is reoxidized upon exposure to the air.

The faculty of entering into the reverse reaction, reduction, with a shift from the colored substance to the colorless one and vice versa, is also possessed by the quinones, the formation of which is quite possible in the given case. Experiment indicates, however, that no quinone is formed in reality, the reaction being accompanied by the formation of azo compounds.

When a chloroamine is reacted with diphenyl amine, a mixture of chlorine-substituted diphenyl amine derivatives is formed, depending upon the quantity of chloroamine used in the reaction. For example, with equimolecular proportions of the reagents, about 10 g. of an oily product, easily soluble in organic solvents and containing 18.6% of bound chlorine, was obtained from 8.8 g. of diphenyl amine. The oil crystallizes upon standing and cooling. After purification, the crystals had a m.p. of 78°C (according to Klaus the m.p. of 4,4-dichloro-diphenyl amine is 80°C).

0.1324 g. substance: 0.1556 g. AgCl.  
 Found %: Cl 29.05.  
 $C_{12}H_{10}Cl_2NH$ . Calculated %: Cl 29.38.

Thus, the crystalline substance that settled out of the oil is dichloro-diphenyl amine, which constitutes the oily mixture together with unchanged diphenyl amine and monochloro-diphenyl amine, partially formed during the reaction.

When twice the amount of chloroamine is used, the dichloro-diphenyl amine is obtained in a quantitative yield. With a threefold excess of chloroamine, tetrachloro-diphenyl amine separates out, in addition to the dichloro-diphenyl amine, as bushes of grouped acicular crystals with a m.p. of 135°C (according to the literature the m.p. of 2,4,2',4'-tetrachloro-diphenyl amine is 133-134°C) and a chlorine content of 45.3% (computed value - 45.63%). The consumption of active chlorine is limited to 4 molecules of the chloroamine; moreover, we were unable to separate out any other products than the chlorine-substituted ones discussed.

#### Action of Chloroamines upon Aliphatic Amines

If a solution of a chloroamine is added to a solution of an aliphatic amine, the mixture grows warm just as in the cases described above for the aromatic amines, and the chloroamine base is regenerated, the quantity of active chlorine in the solution remaining unchanged, while the solution acquires a sharper odor.

The primary and secondary ethyl, butyl, isopropyl, isobutyl, hexyl, and other amines were employed in the reaction. Corresponding to each one of them, we obtained chloroamines as oils with a sharp suffocating smell.

When equimolecular proportions of the reagents were employed, the primary amines yielded monochloroamines; when an excess of the chloroamine was used, we got the dichloroamines.

According to Vassiliades [5], the action of chloroamines upon secondary aliphatic amines ought to yield condensation products of substituted hydrazo compounds, liberating hydrogen chloride, as follows:



This was not borne out by our experiments, however, although they were carried out under the same conditions as those of Vassiliades. No crystalline products of conversion of the original amines were obtained at all: neither hydrazo compounds nor hydrochlorides of the amines; we always obtained dialkyl-chloroamines as oils with corresponding properties and percentages

of active chlorine.

When dry hydrogen chloride was passed through solutions of the chloroamines produced, the latter decomposed quantitatively, being converted into the initial secondary amines as hydrochlorides.

When chloroamines acted upon triethyl amine, we got a chloroamine base as well as a precipitate that was insoluble in hot benzene and gasoline, while active chlorine remained in the solution. After exhaustive washing with hot benzene, the precipitate fused at 253°C. and dissolved easily in water, exhibiting an acid reaction. When the aqueous solution was alkalized, a liquid base with the characteristic odor of the initial amine came to the surface:

0.1175 g. substance: 8.3 ml. 0.1 N, NaOH.  
(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>N·HCl. Calculated: 8.5 ml. 0.1 N NaOH.  
0.2101 g. substance: 15.1 ml. 0.1 N AgNO<sub>3</sub>  
Found %: Cl 25.48.  
(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>N·HCl. Calculated %: Cl 25.77.

Thus, its properties and its analytical data indicate that the precipitate was identical with triethyl amine hydrochloride.

After the precipitate had been filtered out of the solution and the latter distilled, diethyl chloroamine was isolated. In addition, the formation of acetaldehyde was noted in the reaction products by means of its characteristic reactions, especially with Schiff's reagent.

The quantity of diethyl chloroamine formed in this reaction can be easily determined by decomposing it with dry hydrogen chloride, forming a diethyl amine salt. For example, 10 g. of the initial triethyl amine yielded 5.8 g. of triethyl amine hydrochloride as a result of interaction with the chloroamine and 3.9 g. of diethyl amine (by the decomposition of the diethyl chloroamine).

#### Action of Chloroamines upon Aliphatic-Aromatic Amines

a) Reaction with the Benzyl Amines. When chloroamines act upon benzyl amines and dibenzyl amines in a benzene solution, the reaction of double decomposition proceeds smoothly; benzyl and dibenzyl chloroamines are obtained in quantitative yields, and the chloroamine base is regenerated. For example, from 3 g. of benzyl amine we obtained 4 g. of benzyl chloroamine, and from 3 g. of dibenzyl amine 3.4 g. of dibenzyl chloroamine; the characteristic properties of both chloroamines were those previously described by Berg [10] as well as by Chattaway and Orton.

When benzene solutions of the chloroamine and of tribenzyl amine are mixed together, no change is noticed, as in the previous instances; but upon standing the percentage of active chlorine drops, and a crystalline precipitate settles out. When washed out with extractions of hot benzene, the precipitate fuses at 227°C, is soluble in hot water, and is easily decomposed by aqueous solutions of ammonia and soda, forming tribenzyl amine; thus, it is doubtless a tribenzyl amine salt, possessing exactly the same properties as the latter.

If hydrogen chloride is passed into the benzene solution (the filtrate), containing active chlorine, a salt of dibenzyl amine (m.p. 255°C) settles out together with a salt of tribenzyl amine (m.p. 227°C) and the base of the partially unreacted initial chloroamine. The salts were washed with hot benzene and separated by fractional crystallization from alcohol (the tribenzyl amine salt is more insoluble in alcohol and settles out first). Upon decomposition of the salts we obtained dibenzyl amine and tribenzyl amine. To prove the presence of dibenzyl amine, we prepared nitroso dibenzyl amine as acicular crystals with a m.p. of 52°C (agrees with the literature figures).

Upon long standing or upon slight heating the reaction continues to its conclusion (no more of the initial chloroamine is left in the reaction mixture), and the reaction products are isolated in good yields. For example, 15 g. of tribenzyl amine used for the reaction yielded 8 g. of tribenzyl amine hydrochloride and 5.2 g. of dibenzyl amine, separated as a salt after allowing hydrogen chloride to pass through the solution. An aqueous extract of the

reaction products yielded 1.1 g. of benzoic acid, while the formation of benzaldehyde was demonstrated quantitatively.

Thus there is no doubt that tribenzyl amine reacts with the chloroamines exactly as do the aliphatic amines, the benzene ring not being chlorinated thereby.

b) Reaction with Dimethylaniline. Equimolecular quantities of dimethylaniline and chloroamine were mixed in benzene. Three to four hours later the percentage of active chlorine in the solution dropped, the chloroamine base settling out. From the filtrate we obtained a sharp-smelling greenish oil, which when distilled under standard conditions yielded two fractions with b.p. of 206°C and 232°C. According to their boiling points, these substances correspond to the ortho and para isomers of chlorodimethylaniline according to its chlorine content, the product likewise corresponds to chlorodimethylaniline:

0.1950 g. substance: 0.1783 g. AgCl.  
0.2122 g. substance: 0.1946 g. AgCl.  
Found %: Cl 22.62.  
 $C_6H_4ClN(CH_3)_2$ . Calculated %: Cl 22.82

Reaction with nitrous acid yielded two nitroso derivatives in the form of a yellow oil and orange needles with a m.p. of 53°C, which are characteristic of nitroso-o- and nitroso-p-chlorodimethylanilines:

0.0215 g. substance: 1.1537 g. AgCl.  
0.2002 g. substance: 0.1529 g. AgCl.  
Found %: Cl 18.67, 18.90.  
 $C_6H_4Cl(CH_3)_2NO$ . Calculated %: Cl 19.21.

With a twofold or threefold excess of the chloroamine used for the reaction, 2,4-dichlorodimethylaniline (b.p. 234°C, chlorine - 37.8%) and 2,4,6-trichlorodimethylaniline (b.p. 247°C, chlorine - 47%) were obtained, respectively. The quantitative yields of the chlorine-substituted products indicate that here, as in the case of the primary and secondary aromatic amines, the ring is chlorinated, while no oxidizing decomposition, such as occurs with the aliphatic amines and tribenzyl amine, takes place.

#### CONCLUSIONS

Investigation of the reaction of N-Cl amines with amines yielded the following results:

1. In the aromatic amines, both primary and secondary, as well as in the aliphatic-aromatic amines where the nitrogen atom is directly bound to the benzene ring (dimethylaniline), the action of the chloroamines causes the chlorination of the ring (C-chlorination). With an excess of chloroamine the fully chlorine-substituted primary amines are oxidized to azo compounds.
2. In the primary and secondary aliphatic and aliphatic-aromatic amines whose nitrogen is bound to the aliphatic chain and not to the aromatic ring (benzyl amines), the chloramines enter into double decomposition reactions (N-chlorination).
3. When chloroamines act upon tertiary aliphatic amines and upon tribenzyl amine, one alkyl group is split off and oxidized to an aldehyde, and the dialkyl chloroamine formed is chlorinated (at the nitrogen atom).

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# HYDROLYSIS OF 1,2,3-TRICHLOROBUTANE UNDER PRESSURE IN THE PRESENCE OF POTASSIUM CARBONATE

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The problem of hydrolyzing trihalogen derivatives of the hydrocarbons of the  $C_4$  and higher series under pressure has not been investigated as yet.

D. V. Tishchenko [1] demonstrated that "when boiled with a solution of potash only those polychlorides of isopentane saponify whose chlorine atoms are not attached to adjacent hydrocarbons". On the basis of other papers he laid down a rule, according to which the greater the number of chlorine atoms in an aliphatic polychloride and the closer they are to one another, the harder it is to effect saponification. [2]

It was of interest to study the hydrolysis of 1,2,3-trichlorobutane under pressure and to ascertain the possibility of applying Tishchenko's rule to this case. Moreover, the problem under investigation was interesting as one of the possible ways of utilizing butane and the butenic fractions of cracking gases. The object and trend of the present paper were governed by these considerations.

A 10-15% excess of potassium carbonate was employed as the saponifier. The hydrolysis was effected in a rotating autoclave at a temperature of 145-165°C for a period of 25-30 hours.

It was found that no methylglycerol was formed under the reaction conditions. The reaction gives rise to chlorine-containing products, consisting of a mixture of dichlorobutanols and chlorobutanediols.

Comparing our results with those obtained in the hydrolysis under pressure of 1,2- and 2,3-dichlorobutanes [3], we must acknowledge that introducing the third atom of chlorine (adjoining the chlorine-bound carbon) renders the hydrolysis reaction considerably more difficult, which agrees perfectly with Tishchenko's rule.

## EXPERIMENTAL

The raw material was prepared by the dehydration of butanol-1 in the presence of  $Al_2O_3$ , followed by the chlorination of the butenes in the vapor phase.

The dichlorobutanes were isolated by distilling the products of chlorination of the butenes at 90 mm into a column 115 cm. long with an inside diameter of 5 cm., filled with bits of glass tubing. A fraction with a b.p. of 58-60°C was selected; it was further fractionated in the same column at atmospheric pressure.

The fraction obtained by redistillation was entirely stable, all of it boiling within the range 123-125°C.

$d_4^{20}$  1.1251;  $n_D^{20}$  1.4450;  $MR_D$  30.10.  
 $C_4H_8Cl_2$  Calculated  $MR_D$  30.40.  
Found %: Cl 56.2, 56.1.  
 $C_4H_8Cl_2$  Calculated %: Cl 55.9.

The 1,2-dichlorobutane was then subjected to chlorination to trichlorobutane in the liquid phase. Chlorination was done in a glass flask with reflux condenser, fitted with a vigorous agitator and illuminated by a 100 watt lamp. Anhydrous chlorine was added to the liquid until the weight had increased by the calculated amount. The reaction products were washed in a solution of sodium bicarbonate, dried with  $\text{CaCl}_2$ , and distilled, first in vacuum (15 mm.) and then at atmospheric pressure. A fraction with a stable boiling point of 165 - 167°C (759 mm.) [4] was obtained:

$d_4^{15}$  1.3172;  $d_4^{20}$  1.3164;

$n_D^{15}$  1.4745;  $n_D^{20}$  1.4790;  $n_F^{15}$  1.4836.

$MR_C$  35.31;  $MR_D$  34.98;  $MR_F$  35.89.

$\text{C}_4\text{H}_7\text{Cl}_3$ . Calculated:  $MR_C$  35.10;  $MR_D$  35.27;  $MR_F$  35.67.

Found %: C 29.7; H 4.2; Cl 65.7, 65.8.

$\text{C}_4\text{H}_7\text{Cl}_3$ . Calculated %: C 29.7; H 4.4; Cl 65.9.

Hydrolysis of the 1,2,3-trichlorobutane was effected in a rotating autoclave of 0.5 liter capacity at a speed of 60-65 rpm.

The autoclave was charged with 45 g. of trichlorobutane, 60 g. of anhydrous  $\text{K}_2\text{CO}_3$ , and 250 g. of water. The temperature was kept at 160-170°C for 25 to 30 hours. The gaseous reaction products were then removed and the autoclave opened. The aqueous portion was repeatedly treated with ether. The ether extract was desiccated with calcined potash, and the ether driven off over a water bath. The amount of mineralized chlorine was determined before the treatment of the autoclave contents with ether. The amount of  $\text{Cl}^1$  varied from 19.5 to 22.1 g in each test.

Let us cite the results of one typical test. After the ether had been driven off, there remained in the flask 82 g. (from 4 tests), which were distilled at 50 mm. in a herringbone dephlegmator (50 cm. long). When 75 g. were distilled, the following fractions were obtained:

I 35 - 82°C ..... 6 g.

II 82 - 87 ..... 59 g.

III residue in flask .... 5 g.

The fraction with a 82 - 87°C boiling point (at 50 mm.):

$d_4^{20}$  1.1766;  $n_D^{20}$  1.4695;  $MR_D$  33.97; (for  $\text{C}_4\text{H}_9\text{OCl}_2$ ):  $MR_D$  29.58 (for  $\text{C}_4\text{H}_9\text{O}_2\text{Cl}$ ).

$\text{C}_4\text{H}_9\text{OCl}_2$ . Calculated:  $MR_D$  31.93

$\text{C}_4\text{H}_9\text{O}_2\text{Cl}$ . Calculated:  $MR_D$  28.59.

Found %: Cl 44.90, 44.67; OH 12.93, 12.58.

$\text{C}_4\text{H}_9\text{OCl}_2$ . Calculated %: Cl 49.65; OH 10.69.

$\text{C}_4\text{H}_9\text{O}_2\text{Cl}$ . Calculated %: Cl 28.59.

The analytical data indicate that the product under investigation consists of a mixture of dichlorobutanol and chlorobutanediol.

To separate the mixture into its components the chlorobutanediol was washed free of the dichlorobutanol by water. For this purpose 32 g. of the product was vigorously agitated with 60 ml. of water. The bottom layer (insoluble in water) was separated from the aqueous layer and desiccated with calcined sodium sulfate. We obtained 25.3 g. of a substance with b.p. of 82-85°C (50 mm.).

$d_4^{20}$  1.1911;  $n_D^{20}$  1.4670;  $MR_D$  33.3.

$\text{C}_4\text{H}_9\text{OCl}_2$ . Calculated:  $MR_D$  31.93.

Found %: Cl 47.43, 47.16.

$\text{C}_4\text{H}_9\text{OCl}_2$ . Calculated %: Cl 49.65.

Found %: OH 9.77, 9.35

$\text{C}_4\text{H}_9\text{OCl}_2$ . Calculated %: OH 10.69.

Investigation of the Aqueous Solution. The water was driven off under vacuum (100 mm.) and collected in two separate batches. At first, oily drops were distilled over. Both batches were salted out with potash. The top oily layer was drawn off in alcohol and desiccated with calcined sodium sulfate. The alcohol was driven off from the flask by means of a herringbone dephlegmator. Three g. of product were obtained:

$d_4^{20}$  1.0942;  $n_D^{20}$  1.4575;  $MR_D$  31.00.

$C_4H_9O_2Cl$ . Calculated:  $MR_D$  29.59.

	Found %:	Cl 28.15, 28.26.
$C_4H_9O_2Cl$ .	Calculated %:	Cl 28.51.
	Found %:	OH 24.71, 24.68.
$C_4H_9O_2Cl$ .	Calculated %:	OH 27.31.

#### CONCLUSIONS

1. It has been found that when 1,2,3-trichlorobutane is saponified under pressure by an aqueous solution of potash, a mixture of chlorine-containing products (dichlorobutanols and chlorobutanediols) is obtained.
2. Methylglycerol is not formed under the reaction conditions.
3. The hydrolysis reaction of 1,2,3-trichlorobutane under pressure in the presence of an aqueous solution of potash is governed by Tishchenko's rule.

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## RESEARCHES IN THE FIELD OF THE ALIPHATIC NITROSO COMPOUNDS

### VI. PREPARING HALOGEN NITROPARAFFINS FROM THE OXIMES OF ALDEHYDES AND KETONES

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Of late the nitro compounds of the aliphatic series are acquiring increasing importance in various fields of organic synthesis; this was facilitated by the discovery of the relative ease with which they could be produced industrially. The halogen nitro compounds, containing a halogen atom attached to the same carbon atom as the nitro group, occupy a special place among the nitro compounds.

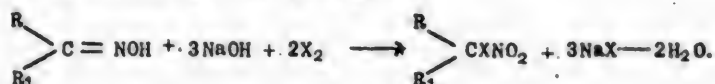
These compounds, as one of the present authors has already noted, possess a number of interesting properties; in particular, they may be employed as oxidants in various reactions [1]. In the last few years some substances of this type have proved their worth as fumigants against various insect pests [2], being more effective than many other compounds.

Halogen nitro compounds can be produced either by the oxidation of the corresponding halogen dinitroso compounds by nitric acid [3] or by the halogenation of the nitroparaffins in an alkaline medium [4,5,6]. The literature also contains an indication of the feasibility of preparing some halogen nitroso compounds by the halogenation of the oximes of ketones [7]; this statement refers, however, chiefly to the cyclic compounds of the terpene groups.

The literature contains contradictory statements concerning the preparation of aliphatic halogen nitroso compounds [8]. At the same time the given method is of considerable interest, and its application to compounds of the aliphatic series would make it possible to prepare halogen nitro compounds of any desired structure.

In connection with the foregoing we undertook experiments looking to the synthesis of halogen nitroparaffins by the halogenation of the oximes of ketones and aldehydes in an alkaline medium. It should be noted that the method of halogenation of ketonic oximes was successfully employed in the preparation of halogen nitroso-paraffins [3]. Halogenation of the oximes of aldehydes and ketones was done under cooling in an alkaline medium, 4 moles of caustic soda being used per mole of oxime.

Halogenation of the following oximes was studied: of acetaldehyde, heptyl alcohol, acetone, methyl ethyl ketone, and methyl propyl ketone. In every case, with the exception of the oxime of heptyl alcohol, we obtained the corresponding nitro compound, the yield falling within the range of 30-65%. The reaction for the formation of halogen nitro paraffins may be represented by the following summary diagram.



This reaction apparently takes place in three steps; in the first stage the halogen is added to the oxime, the halogen nitroso compound being obtained after the hydrogen halide is



split off from the addition product. The halogen nitro paraffin is formed as the result of the oxidation of the hypochlorite or hypobromite of the halogen nitroso paraffin. During the subsequent course of the reaction between the oximes and the halogens, the observations of various investigators concerning the preparation of halogen nitroso paraffins are confirmed [8-9].

#### EXPERIMENTAL

##### 1. Preparation of Bromonitroethane.

To a solution of 3 g. of the oxime of acetaldehyde and 8.16 g. of caustic soda in 30 ml. of water at a temperature of from 2 °C to 5°C there are added, with constant stirring, 16 g. of bromine. The product obtained is extracted with ether. The ether solution is desiccated with calcium chloride, and the ether is driven off. The residue is distilled in vacuum. B.P. - 40°C at 18 mm.

$$n_D^{18} 1.4785; d_4^{18} 1.732; MR_D 25.14 \\ C_2H_4NO_2Br. \text{ Calculated: } MR_D 24.81$$

According to the literature, bromonitroethane has a b.p. of 69-75°C at 50 mm and of 146-147°C at 760 mm [9]. Yield: about 1 g.

##### 2. Preparation of 2-chloro-2-nitropropane

Chlorine is passed through a solution of 9 g. of acetoxime and 12.3 g. of caustic soda in 125 ml. of water chilled to 1-3°C. As the reaction proceeds a yellow oil collects at the bottom of the reaction vessel. After the reaction is concluded, the oil obtained is dissolved in ether, and the ether solution is desiccated with calcium chloride. After the ether has been driven off, the residue is distilled in vacuum. B.p. 35°C at 15 mm. Yield: 6.7 g.

$$n_D^{19} 1.4378; d_4^{19} 1.230; MR_D 26.34. \\ C_3H_7NO_2Cl. \text{ Calculated: } MR_D 26.54.$$

According to the literature, 2-chloro-2-nitropropane has a b.p. of 69-76°C at 50 mm [4].

##### 3. Preparation of 2-chloro-2-nitrobutane.

Under the conditions of Experiment 2 we obtained 8.8 g. of 2-chloro-2-nitrobutane from 8.6 g. of the oxime of methyl ethyl ketone and 30 g. of caustic soda in 300 g. of water after chlorination and subsequent treatment. B.p. 50-52°C at 17 mm.

$$n_D^{20} 1.4399; d_4^{20} 1.1725; MR_D 30.87. \\ C_4H_9NO_2Cl. \text{ Calculated: } MR_D 31.15.$$

##### 4. Preparation of 2-bromo-2-nitrobutane.

To a mixture of 80 ml. of a 10% aqueous solution of caustic soda and 4.4 g. of the oxime of methyl ethyl ketone there are added 15.8 g. of bromine, the mixture being chilled and well agitated.

After the reaction is concluded, the product obtained is extracted with ether, and the ether extract is washed several times with water and then desiccated with calcium chloride. After the ether has been driven off, the residue is distilled in vacuum. B.p. 45°C at 10 mm. Yield: 5 g.

$$n_D^{18} 1.4724; d_4^{18} 1.523; MR_D 33.49. \\ C_4H_9NO_2Br. \text{ Calculated: } MR_D 33.9.$$

According to the literature, 2-bromo-2-nitrobutane has a b.p. of 78°C at 30 mm and a  $d_4^{20}$  of 1.5364 [4].

##### 5. Preparation of 2-chloro-2-nitropentane.

Under the conditions of Experiment 2 we obtained 2.6 g. of 2-chloro-2-nitropentane

from 2.5 g. of the oxime of methyl propyl ketone and 10 g. of caustic soda in 100 ml. of water after chlorination and suitable subsequent treatment. B.p. 70°C at 25 mm.

$n_D^{20}$  1.4380;  $d_4^{20}$  1.105;  $M_R$  36.01.  
 $C_5H_{10}NO_2Cl$ . Calculated:  $M_R$  36.34.

According to the literature, 2-chloro-2-nitropentane boils at 72°C at 22 mm. [4].

#### 6. Preparation of 2-bromo-2-nitropentane.

Under the conditions of Experiment 4 we obtained about 2 g. of 2-bromo-2-nitropentane from 5 g. of the oxime of methyl propyl ketone and 8 g. of caustic soda in 80 ml. of water and 15.5 g. of bromine. B.p. 92-95°C at 20 mm.

$n_D^{20}$  1.4590;  $d_4^{20}$  1.282.  
0.0442 g., 0.0985 g. substance: 0.0419 g., 0.0941 g. AgBr.  
Found %: Br 40.94, 40.66.  
 $C_5H_{10}NO_2Br$ . Calculated %: Br 40.87.

#### CONCLUSIONS

It has been shown that halogen nitro paraffins can be prepared by the halogenation of the oximes of aldehydes and ketones in an alkaline medium without the preliminary isolation of the halogen nitroso compounds. This method can be employed in the synthesis of halogen nitroparaffins of any desired structure.

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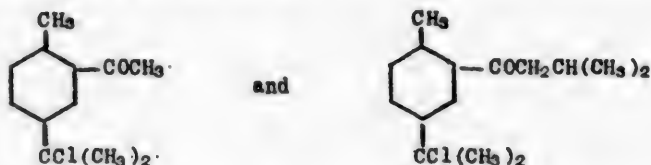
Entered June 22, 1947.

# THE ACTION OF PHOSPHORUS PENTACHLORIDE ON METHYL CYMYL AND ISOBUTYL CYMYL KETONE

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As we know, when phosphorus pentachloride acts upon ketones, the oxygen of the carbonyl group is usually replaced by halogens, resulting in the formation of dihalogen derivatives, with the halogens attached to the same carbon atom. Starting with this, we endeavored to convert methyl cymyl ketone and isobutyl cymyl ketone into the corresponding dichloro derivatives by the action of phosphorus pentachloride, and from the latter to prepare 1-methyl-4-isopropyl-phenyl-acetylene and 1-methyl-4-isopropyl-phenyl-isopropyl-acetylene with the aid of sodium amide. Our research indicated, however, that the cymyl ketones behave anomalously toward phosphorus pentachloride. In the cymyl ketones the latter does not chlorinate the carbonyl group, but the isopropyl group; as a result, we get the following compounds, corresponding to the research of A.E. Favorsky [1]:



The structure of the cited compounds was confirmed by us by way of the following data: determination of the percentage of chlorine, molecular refraction, preparation of semicarbazones containing chlorine, oxidation to a monobasic acid containing chlorine and the semicarbazone formed, as well as by preparation of the nitro derivatives possessing the characteristics of tertiary nitro compounds.

## EXPERIMENTAL

### I. Action of Phosphorus Pentachloride upon Methyl Cymyl Ketone

The methyl cymyl ketone was prepared by the Friedel-Crafts reaction from cymene and acetic anhydride in the presence of aluminum chloride [2,3]. The quantities used in chlorination were 30 g. of methyl cymyl ketone (1/6 g.-mol.) and 35.4 g. of phosphorus pentachloride (1/6 g.-mol.). The phosphorus pentachloride was placed in a flask chilled by snow, to which a reflux condenser was attached. A small amount of the cymyl ketone was poured into the upper opening of the condenser. No outward indications of reaction were observed, while the phosphorus pentachloride remained unchanged. As the ketone was poured in, the flask was heated on a 60°C water bath for 10 hours, and then on a boiling water bath for 5 hours. During the heating large amounts of hydrogen chloride were liberated, the criterion of the termination of heating being the cessation of this liberation of HCl, which lasted for 15 hours. Upon

cooling the product was treated with ice water; the oily layer that separated out was removed, washed with water, and dessicated with calcium chloride. The following fractions were collected when this oily liquid was distilled in vacuum:

- I. b.p. 116-120°C at 15 mm . . . 20 g.
- II. b.p. 120-125 at 15 mm . . . 30 g.
- III. Residue . . . . . 4 g.

The second fraction is the chlorine derivative, whose yield is 70% of the ketone.

In another instance, the mixture was not separated with water after the phosphorus pentachloride had acted on the ketone, but was subjected to vacuum distillation after the halogen phosphorus compounds had been driven off up to 120°C. This yielded the following fractions:

- I. b.p. 115-120°C at 15 mm . . . 10 g.
- II. b.p. 120-125 at 15 mm . . . 39 g.
- III. b.p. 125-130 at 15 mm . . . 3 g.
- IV. Residue . . . . . 2 g.

The yield of chlorine derivative in this case was higher, amounting to 90% of the ketone. The chlorine derivative is a colorless lachrymatory liquid with a sharp odor. B.p. 120-125°C at 15 mm.

$d_4^{25}$  0.946;  $n_D^{25}$  1.480;  $M_R^D$  59.1.

$C_{12}H_{15}OCl$ . Calculated:  $M_R^D$  60.3.

The chlorine was determined by fusion with  $Na_2CO_3 + KNO_3$ .

0.2053 g. substance: 0.1383 g.  $AgCl$ .

Found %: Cl 16.70

$C_{12}H_{15}OCl$ . Calculated %: Cl 16.66.

It should be noted that the Stepanov method did not yield satisfactory results; the chlorine content was below 10%. The chlorine-containing ketone prepared from semicarbazide in the presence of potassium acetate yielded a semicarbazone with a m.p. of 235°C. The halogenated ketone was oxidized by boiling with nitric acid (sp. gr. 1.5) diluted with three volumes of water (5 ml. of  $HNO_3$  were used for 2 g. of the ketone) for a period of 6 hours in a flask fitted with a reflux condenser.

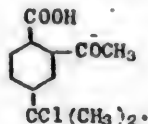
Upon cooling a crystalline substance separated out, which was washed with water. The substance was purified by dissolving it in an alkali and precipitating it from the alkaline solution by dilute sulfuric acid. The dried-out crystals, which do not fuse, decompose at 180°C. With semicarbazide the substance forms a semicarbazone, which indicates that the ketone group was not changed during oxidation. The melting point of the semicarbazone is 235°C. The acid contains chlorine, which was determined by fusion with  $Na_2CO_3 + KNO_3$ .

0.2133 g. substance: 0.1240 g.  $AgCl$ .

Found %: Cl 14.20.

$C_{12}H_{13}O_3Cl$ . Calculated %: Cl 14.58.

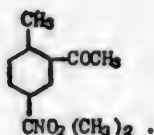
Thus nitric acid oxidized the methyl group; i.e., the following acid was obtained:



To confirm the assumption that the chlorine is attached to the isopropyl group of the cymene, a nitro derivative was prepared in the following manner: to begin with, the chlorine is replaced by iodine by heating the substance with sodium iodide in an acetone solution, thus precipitating sodium chloride; after the acetone is removed, 15 g. of

the iodohydrin is heated with 11 g. of silver nitrite for 1.5 hours. This yields 5 g. of a nitro derivative with a b.p. of 94°C at 25 mm. The presence of nitro groups is proved by the Mulliken and Barker reaction [+]. The nitro compound obtained yielded a negative reaction with nitrous acid for the primary and secondary nitro compounds, as well as for the aromatic nitro compound (regeneration and diazotization), which indicates the presence of nitro groups attached to the isopropyl radical. Thus the formula for the nitro compound ought to be:





## II. Action of Phosphorus Pentachloride Upon Isobutyl Cymyl Ketone

The ketone was prepared by the Friedel and Crafts reaction from cymene (180 g.) and isovaleryl chloride (40 g.) in the presence of aluminum chloride (45 g.). The ketone yield was 40% of the theoretical value. B.p. 270-272°C,  $d^{15}_D$  0.944. For chlorination 40 g. of the ketone (1/18 gr.-mol) and 32 g. of phosphorus pentachloride (1/18 gr.-mol.) were used. The chlorination of the isobutyl cymyl ketone was done exactly like that of the methyl cymyl ketone. Upon distillation of the chlorination product the following fractions were collected:

- I. b.p. 70-76°C at 30 mm..... 5 g.
- II. b.p. 76-80°C at 30 mm..... 40 g.
- III. b.p. 80-100°C at 30 mm..... 10 g.
- IV. Residue ..... 5 g.

Upon redistillation of Fraction II 32 g. of a substance with a b.p. of 78°C at 30 mm was isolated. The yield of the chlorine derivative was about 70% in terms of the initial ketone. The chlorine-containing ketone is a colorless liquid with an acrid smell.

$d^{15}_D$  0.821;  $n^{15}_D$  1.501;  $MR_D$  74.1.

$\text{C}_{15}\text{H}_{21}\text{OCl}$ . Calculated:  $MR_D$  73.4.

The chlorine content was determined by fusion with  $\text{Na}_2\text{CO}_3 + \text{KNO}_3$ .

0.1350 g. substance: 0.0783 g.  $\text{AgCl}$ .

Found %: Cl 14.60.

$\text{C}_{15}\text{H}_{21}\text{OCl}$ . Calculated %: Cl 13.87.

With semicarbazide a semicarbazone containing chlorine was obtained in the form of crystals with a m.p. of 229°C. Upon oxidation of this substance with nitric acid under the conditions set forth earlier, we obtained an acid that contained chlorine and yielded a semicarbazone that did not fuse, but decomposed at 180°C.

To prove the presence of chlorine in the isopropyl group of the ketone, the latter was converted into an iodohydrin and then into a nitro compound with a b.p. of 86°C at 25 mm. The presence of a nitro group attached to the tertiary carbon was proved as in the earlier case.

## CONCLUSIONS

Phosphorus pentachloride, when combined with methyl cymyl ketone and isobutyl cymyl ketone forms chlorine-substituted ketones that contain chlorine attached to the isopropyl radical.

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# SYNTHESIS OF POLYCYCLIC HYDROAROMATIC KETONES

## II. 3-KETO-7-1,2,3,9,10,11-HEXAHYDROPHENANTHRENE

G. T. Tatevosyan and A. G. Vardanyan

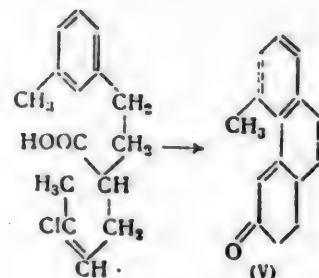
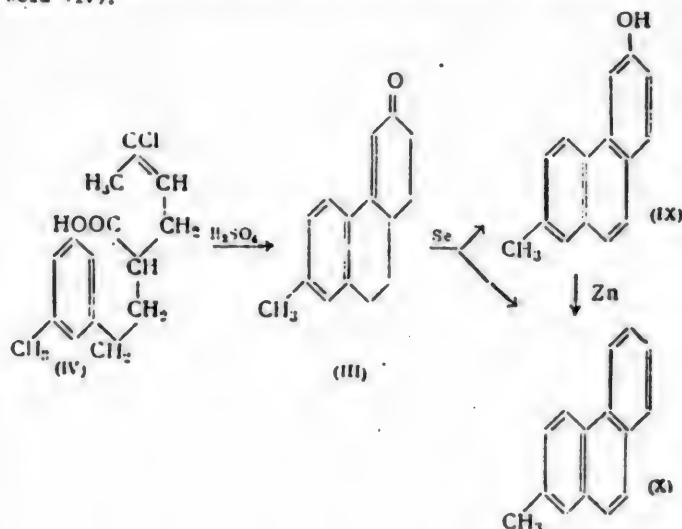
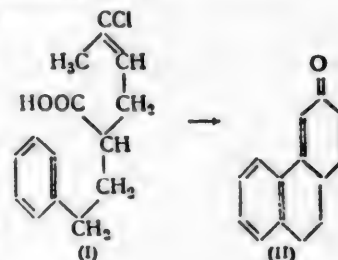
Chemical Institute of the Academy of Sciences of the Armenian SSR.

In our communication I [1] it was shown that  $\alpha$ -(3-chlorocrotyl)- $\gamma$ -phenylbutyric acid (I) is hydrolyzed at the chlorine atom located at the ethylene bond by hot concentrated sulfuric acid, undergoing subsequent double cyclization with the formation of 3-keto-1,2,3,9,10,11-hexahydrophenanthrene (II).

It was likewise pointed out that this type of conversion of  $\alpha$ -(3-chlorocrotyl)- $\gamma$ -arylbutyric acids could be employed in the synthesis of a number of polycyclic hydroaromatic ketones.

The natural derivatives of phenanthrene -- the steroids -- always contain a substituting functional group at the 7 position. It therefore seemed of interest to prepare the isomer, with a methyl group at the 7 position, that is, keto-7-methyl-1,2,3,9,10,11-hexahydrophenanthrene (III), from the homologs of 3-ketohexahydrophenanthrene that had been methylated in the aromatic ring. The present communication deals with this synthesis.

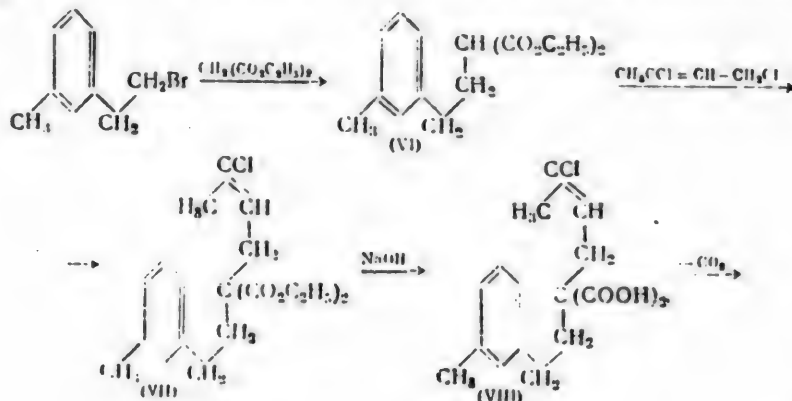
The starting point for the synthesis of this ketone was  $\alpha$ -(3-chlorocrotyl)- $\gamma$ -(*m*-tolyl)-butyric acid (IV):



The cyclization of the meta substituted  $\gamma$ -aryl butyric acids is usually effected at the para position by the substituent within the ring. In the literature, however, only solitary instances of partial ortho substitution [2] are described, and hence the possibility of a different course of the reaction had to be envisaged,

with the formation of 3-keto-5-methyl-1,2,3,9,10,11-hexahydrophenanthrene as the end product (V).

The acid (IV) was prepared from 3-(*m*-tolyl)-ethyl bromide and 1,3-dichlorobutene-2 by the malonic ester synthesis



3-keto-7-methyl-hexahydrophenanthrene was prepared by the action of acid (IV) on sulfuric acid of sp. gr. 1.8, at 70-75°C. with a yield of 60-61%. The structure of the cyclic ketone was determined by means of its dehydrogenation with selenium. The principal dehydrogenation product obtained was 3-hydroxy-7-methyl-phenanthrene (IX), not previously described in the literature, together with a small amount of 2-methylphenanthrene (X), which was identified as the picrate. 2-methylphenanthrene was likewise prepared by the reduction of 3-hydroxy-7-methylphenanthrene by zinc dust, as was demonstrated by the structure of the latter.

Thus, the product of the sulfuric acid hydrolysis and the double ring formation of  $\alpha$ -(3-chlorocrotyl- $\gamma$ -(*m*-tolyl)-butyric acid was found to be, as had been expected, 3-keto-7-methyl-1,2,3,9,10,11-hexahydrophenanthrene.

#### EXPERIMENTAL

The initial  $\beta$ -(*m*-tolyl)-ethyl alcohol was prepared by the interaction of ethylene oxide and *m*-tolyl magnesium iodide [3].

$\beta$ -(*m*-tolyl)-ethyl bromide, previously prepared by Bogert and Apfelbaum [3] by the action of phosphorus tribromide upon the alcohol, was prepared by means of a mixture of hydrobromic and sulfuric acids. The mixture of 107.5 g. of  $\beta$ -(*m*-tolyl)-ethyl alcohol, 342 g. of 48% hydrobromic acid, and 100 g. of concentrated sulfuric acid was boiled for 3.5 hours, after which an equal quantity of water was added. The layer of bromide that separated out was separated from the water by means of ether; the ether solution was washed with dilute alkali and then with water, after which it was desiccated over calcium chloride. After the ether had been driven off, the residue was twice distilled in vacuum. 120 g. (76.3% of theoretical) of the bromide, boiling at 88-90°C (4 mm.), was obtained.

$\beta$ -(*m*-tolyl)-ethyl malonate (VI). To sodium malonic ester, prepared from 145 g. of malonic ester, 17 g. of sodium, and 280 ml. of absolute alcohol, there was added 120 g of  $\beta$ -(*m*-tolyl)-ethyl bromide, while the mixture was being stirred. After standing for half an hour at room temperature the mixture was boiled for 3 hours, after which it was allowed to stand overnight. Most of the alcohol was driven off from the reaction mixture; water acidulated with hydrochloric acid was added to the residue; benzene was used to remove the layer of reaction product that separated out from the water; and the benzene solution was washed with water and then desiccated with dehydrated sodium sulphate. The oil remaining after the benzene had been driven off was twice distilled in vacuum. We obtained 142.7 g. (85.1% of the theoretical quantity) of a colorless oil, boiling at 150-152°C (3 mm.) and 171-172°C (6 mm.):

$d_4^{15}$  1.0544;  $n_D^{15}$  1.4900;  $MR_D$  76.24.

$C_{16}H_{22}O_4F_3$ . Calculated:  $MR_D$  75.79.

0.0970 g. substance: 0.2450 g.  $CO_2$ ; 0.0710 g.  $H_2O$ .

found %: C 68.86; H 8.14.

$C_{16}H_{22}O_4$ . Calculated %: C 69.06; H 7.71

$\beta$ -(*m*-tolyl)-ethyl- $\gamma$ -chlorocrotyl-malonate (VII). To a solution of the sodium derivative of the ester (VI), prepared from 120 g. of the ester, 11 g. of sodium and 200 ml. of absolute alcohol there was gradually added, with constant stirring and water cooling, 65 g. of freshly distilled 1,3-dichlorobutene-2. The mixture was boiled for 5 hours, after which the alcohol was driven off and enough water acidulated with hydrochloric acid was added to dissolve the salt formed. The oil that separated out was dissolved in benzene, and the benzene solution washed with water and desiccated with dehydrated sodium sulfate. After the solvent was driven off, the residue was distilled in vacuum. We obtained 149.5 g. (93.2% of the theoretical amount) of a slightly yellowish thick oil that boiled at 191-194°C (3 mm.):

$d_4^{17}$  1.0974;  $n_D^{17}$  1.5000;  $MR_D$  98.28.

$C_{20}H_{27}O_4ClF_4$ . Calculated:  $MR_D$  98.66.

0.1162 g. substance: 0.0458 g. AgCl.

0.1224 g. substance: 0.0490 g. AgCl.

Found %: Cl 9.76, 9.90.

$C_{20}H_{27}O_4Cl$ . Calculated %: Cl 9.69.

$\beta$ -(*m*-tolyl)-ethyl- $\gamma$ -chlorocrotyl-malonic acid (VIII). A mixture of 90 g. of the ester (VII), 30 g. of caustic soda, and 410 ml. of ethyl alcohol was boiled for 4 hours with a reflux condenser, after which 200 ml. of water was added, and all the alcohol driven off. To the chilled residue there was added 130 g. of concentrated hydrochloric acid. The heavy oil that separated out upon acidification was dissolved in ether, and the ether solution was washed with water and desiccated with anhydrous sodium sulfate. After elimination of the ether the residue was fully crystallized. We obtained 75.5 g. (76.2% of the theoretical amount) of a yellow raw material. After recrystallization from water, the acid (VIII) was obtained in the form of light, colorless crystals that fuse at 155-156°C. The substance dissolves easily in alcohol and ether, but is slightly soluble in hot water and wholly insoluble in cold water.

0.1039 g. substance: 0.0494 g. AgCl.  
 0.1299 g. substance: 0.0594 g. AgCl.  
 Found %: Cl 11.76, 11.34.  
 $C_{16}H_{19}O_4Cl$ . Calculated: % Cl 11.49.

$\alpha$ -(3-chlorocrotyl)- $\gamma$ -(*m*-tolyl)-butyric acid (IV). 74.5 g. of the dibasic acid (VIII) was decomposed by heating in a small Cluizen flask. After no more carbon dioxide was liberated, the residue was distilled in vacuum. We obtained 60.5 g (94.62% of the theoretical amount) of a yellowish, extremely viscous oil, boiling at 193-196°C:

$d_{20}^{20}$  1.1081;  $n_D^{20}$  1.5266;  $M_R^D$  73.89.  
 $C_{15}H_{19}O_2Cl$  F<sub>4</sub>. Calculated:  $M_R^D$  73.80.  
 0.1484 g. substance: 0.0810 g. AgCl.  
 0.1296 g. substance: 0.0708 g. AgCl.  
 Found %: Cl 13.59; 13.50.  
 $C_{15}H_{19}O_2Cl$ . Calculated %: Cl 13.54.

3-keto-7-methyl-1,2,3,9,10,11-hexahydrophenanthrene (III). To 21 g. of the acid (IV), chilled in ice and constantly stirred, there was gradually added 115 ml. of sulfuric acid, sp. gr. 1.8. The addition of the acid was accompanied by the abundant liberation of hydrogen chloride. After standing for half an hour at room temperature, the mixture was heated to 70-75°C for five hours in a current of carbon dioxide and then allowed to stand overnight.

The following day the mixture was decanted over ice; the viscous oil that separated out was dissolved in ether, the ether solution was twice washed in alkali and then in water, and then desiccated with anhydrous sodium sulfate. After the ether had been driven off, the residue was completely crystallized. We obtained 10.18 g. (60.95% of the theoretical amount) of a colorless substance, recrystallized from alcohol, that boiled at 95-96°C. The substance bleaches bromine vapors and deoxidizes an alkaline solution of potassium permanganate.

0.0966 g. substance: 0.3054 g. CO<sub>2</sub>; 0.0650 g. H<sub>2</sub>O.  
 0.1018 g. substance: 0.3178 g. CO<sub>2</sub>; 0.0700 g. H<sub>2</sub>O.  
 Found %: C 85.19, 85.16 H 7.45, 7.63.  
 $C_{15}H_{16}O$ . Calculated %: C 84.90; H 7.55.

When the substance is allowed to stand with a solution of semicarbazide, a light-yellow, finely crystalline semicarbazone is formed, which is only very slightly soluble in alcohol, ether, and benzene. After recrystallization from boiling benzene, the semicarbazone fuses with decomposition at 221-222°C.

The oxime of the ketone was prepared by boiling a mixture of 2 g. of the substance, 1.16 g. of hydroxylamine chloride, 1.8 g. of barium carbonate, and 30 ml. of alcohol for five hours. The residue that settled out when the filtrate was chilled was filtered, washed with water, and recrystallized from alcohol. The colorless light crystals of the oxime fuse with decomposition at 161-162°C.

Dehydrogenation. 5.97 g. of the ketone were heated with 4.5 g. of selenium for 3.5 hours in a small Cluizen flask. The temperature was kept at 290-320°C, and raised to 340-350°C toward the end of the experiment. The thick oil, which was decanted while hot into a porcelain dish, crystallized almost completely upon standing. The product of dehydrogenation was boiled for 20 minutes with 100 ml. of a 10% solution of caustic potash, most of the



substance dissolving, while the undissolved oil gradually solidified upon cooling. The mixture was filtered, and the undissolved substance remaining on the filter was dried and distilled in vacuum. 0.59 g. of a colorless substance with a m.p. of 54-55°C (2-methylphenanthrene<sup>[4]</sup>) was obtained from the crystalline distillate after recrystallization from alcohol (the solution possessed a violet-blue fluorescence). When an alcoholic solution of picric acid acted upon the substance an orange-yellow picrate was formed, melting at 117-118°C (the picrate of 2-methylphenanthrene <sup>[4]</sup>).

The alkaline filtrate containing the acid product of dehydrogenation (3-hydroxy-7-methylphenanthrene) was washed with benzene to remove any traces of oil, after which the benzene residue was eliminated by boiling. Upon acidification with a chilled solution of hydrochloric acid an oil separated out that quickly crystallized. The sediment was filtered, washed with water, dried, and weighed (2.73 g.). The substance was then distilled in vacuum at 200-201°C (3 mm.). The yellowish distillate yielded, after recrystallization from alcohol, a substance with a m.p. of 146-147°C.

0.0936 g. substance: 0.2972 g. CO<sub>2</sub>; 0.0488 g. H<sub>2</sub>O.  
Found %: C 86.59; H 5.77.  
C<sub>16</sub>H<sub>12</sub>O. Calculated %: C 86.54; H 5.77.

When treated with picric acid, 3-hydroxy-7-methylphenanthrene forms the orange-yellow picrate, melting with decomposition at 154-155°C.

4.460 mg. substance: 0.366 ml. N<sub>2</sub> (22°C 741 mm.)  
Found %: N 9.28.  
C<sub>16</sub>H<sub>12</sub>O · C<sub>6</sub>H<sub>3</sub>O<sub>7</sub>N<sub>3</sub>. Calculated %: N 9.61.

A mixture of 1.8 g. of the substance and 18 g. of zinc dust was heated to dull-red heat in a quartz test tube. The reduction product was condensed on the cold walls of the test tube in the form of oily green drops, which crystallized completely after the end of the test. The colorless substance produced by double recrystallization from alcohol had a m.p. of 52-53°C. A test mixture of the substance with a preparation of 2-methylphenanthrene, which melts at 54-55°C, fused without depression (52-54°C). The picrate of the reduction product had a m.p. of 116-117°C.

#### CONCLUSIONS

The interaction of sulfuric acid and α-(3-chloroacetyl)-γ-(*m*-tolyl)-butyric acid, prepared by malonic-acid synthesis from β-(*m*-tolyl)-ethyl bromide and 1,3-dichlorobutene-2 was studied.

It has been shown that α-(3-chloroacetyl)-γ-(*m*-tolyl)-butyric acid undergoes hydrolysis and double ring formation under the action of sulfuric acid, forming 3-keto-7-methyl-1,2,3,9,10,11-hexahydrophenanthrene. By dehydrogenation of this ketone over selenium 2-methylphenanthrene was prepared, together with 3-hydroxy-7-methylphenanthrene, not previously described in the literature. 3-hydroxy-7-methylphenanthrene was reduced by zinc dust to 2-methylphenanthrene.

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## SYNTHESIS OF POLYCYCLIC HYDROAROMATIC KETONES

### III. 3-KETO-1, 2, 3, 11, 12, 12a-HEXAHYDROCHRYSENE.

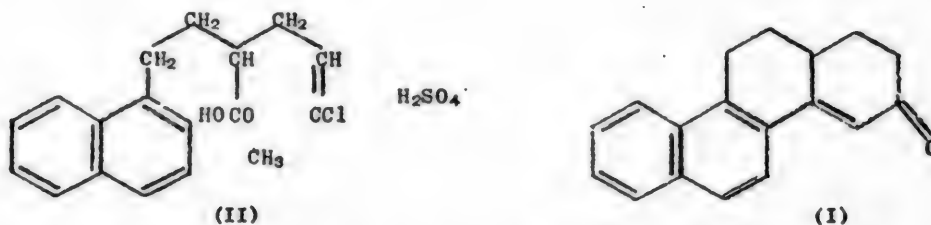
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In 1940, Goldberg and Monnier [1] demonstrated that some compounds of the D-homoandrostane series possess androgenic activity that approaches the activity of the corresponding natural hormones. Somewhat later Bachmann and Holmes [2] found that the estrogenic activity of isomeric D-equilenin differs but little from that of the corresponding equilenins. The observations of these researchers gave an impulse to extensive study of the D-homosteroids, the problem of whose synthesis is the subject of a large number of researches and patent claims.

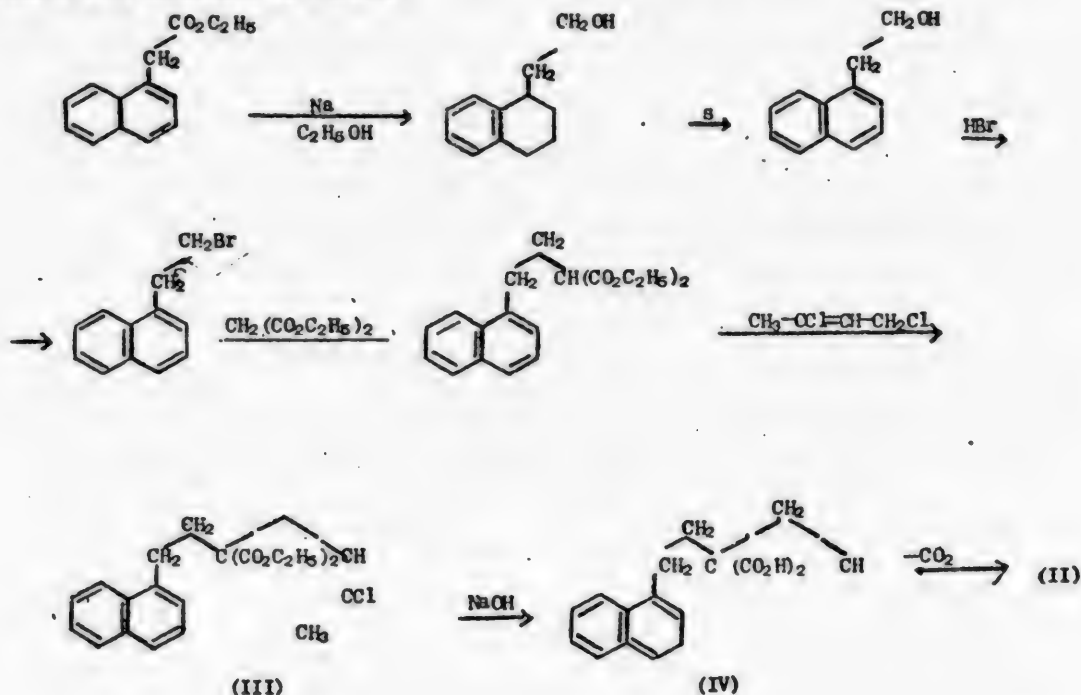
Ketones with the same cyclic structure may be used as starting products for the synthesis of compounds whose structure approaches that of the D-homosteroids, which are derivatives of the partial or complete hydrogenation of chrysene. The idea therefore arose of applying the method of synthesizing polycyclic ketones previously developed [3], consisting of sulfuric-acid hydrolysis and double cyclization of  $\alpha$ -(3-chlorocrotyl)- $\gamma$ -aryl butyric acids to ketones with the cyclic system of chrysene. The present communication describes the synthesis of one of the ketones of this series: 3-keto-1,2,3,11,12,12a-hexahydrochrysene (I). This ketone had already been synthesized by Wilds and Shunk [4] from 1-keto-2-carbethoxy-1,2,3,4-tetrahydrophenanthrene and  $\beta$ -diethyl-aminoethyl-methyl ketone by the Mannich-Robinson method.

We proposed to prepare 3-keto-1,2,3,11,12,12a-hexahydrochrysene by the action of sulfuric acid on  $\alpha$ -(3-chlorocrotyl)- $\gamma$ -(1-naphthyl)-butyric acid (II):



In the cyclization of  $\gamma$ -(1-naphthyl)-butyric acids by the Friedel-Crafts reaction, in exceptional instances the closing of the ring at the peri position, leading to the formation of a seven-membered ring, takes place, as we know, with either unsaturated substituents that oppose ortho cyclization or ethylene bonds [5] present in the side chain, or under the influence of activating substituents in the naphthalene ring [6]. When these acids are cyclized by sulfuric acid, the closing of the ring at the peri position has not been observed up to the present time; hence the feasibility of peri cyclization with the formation of a polycyclic system containing one seven-membered ring had to be considered practically out of the question in this case.

Acid (II) was prepared from  $\beta$ -(1-naphthyl)-ethyl bromide and 1,3-dichlorobutene-2 by the malonic acid synthesis as follows:



As indicated in the diagram, the initial  $\beta$ -(1-naphthyl)-ethyl bromide was prepared by the dehydrogenation of  $\beta$ -(1-tetralyl) ethanol. The dehydrogenation of this alcohol in the presence of a palladium catalyst was investigated by Norman and O'Leary [7]. It was found that at 280-303°C the dehydrogenation of the ring is accompanied by the destruction of the side chain, carbon monoxide and hydrogen being liberated:



The basic product of dehydrogenation was  $\alpha$ -methylnaphthalene. The naphthylethanol formed totaled only 12%.

Our efforts to dehydrogenate  $\beta$ -(1-tetralyl)-ethanol with selenium at 300-320°C proved that under these conditions the aromatization of the ring is accompanied by the dehydration of the alcohol. The  $\alpha$ -vinyl naphthalene formed during this reaction is apparently largely reduced by the hydrogen selenide to  $\alpha$ -ethyl naphthalene. The product of dehydrogenation was not subjected to detailed investigation, and hence the question of the relative quantities of  $\alpha$ -vinyl and  $\beta$ -ethyl naphthalene in the dehydrogenation product remained unexplored, owing to the closeness of their physical properties as well as of the melting points of their picrates.

It was to have been expected that if sulfur, which dehydrogenates at much lower temperatures, were employed, the side chain of the alcohol to be dehydrogenated would remain unaffected. And in fact, when sulfur was used for dehydrogenation at 185-215°C, in spite of the formation of considerable quantities of black, tarry substances containing sulfur, we obtained about 66% of the theoretical amount of  $\beta$ -(1-naphthyl)-ethyl alcohol as a yellowish, noncrystallizing oil, which was converted into the corresponding bromide without further purification.

We prepared 3-keto-1,2,3,11,12,12a-hexahydrochrysene with a yield of 76% by the action of 84.5% hot sulfuric acid upon the acid (II) synthesized as outlined above.

# EXPERIMENTAL

$\beta$ -(1-tetraallyl)-ethanol was prepared by the method outlined by J.V. Braun and J. Reutter<sup>[9]</sup> involving the reduction of 55 g. of  $\alpha$ -naphthyl ethyl acetate by 66 g. of sodium in absolute alcohol, boiling, (480 ml.). We obtained 29.07 g. of alcohol (64.88% of theoretical), possessing the following properties: b.p. 157-158.5°C at 9-10 mm.;  $d_4^{20}$  1.0640;  $n_D^{20}$  1.5633.

Dehydrogenation of  $\beta$ -(1-tetraallyl)-ethanol by selenium. A mixture of 6.42 g. of the alcohol and 5.76 g. of pulverized selenium were heated in a small distillation flask, stiffened with a cross tube at the top, at 300-320°C. At this temperature water was observed to separate out, settling on the walls of the outlet tube in small drops. The heating was continued for 5 hours until no more hydrogen selenide was formed. The reaction product was distilled off at atmospheric pressure; the bulk of the contents distilled over at 250-260°C. After distillation was complete the temperature was raised to 280°C, a small quantity of viscous oil being distilled over. After redistillation we obtained 2.45 g. (43.5% of the theoretical value, in terms of ethyl naphthalene) of a pale green liquid that boiled at 250-255°C. We obtained 0.76 g. of the viscous, high-boiling product.

When the bulk product of dehydrogenation was mixed with an alcoholic solution of picric acid, an abundant precipitate of an orange-yellow picrate was formed, which fused at 98°C after recrystallization. The properties of the dehydrogenation product are compared with those of  $\alpha$ -vinyl and  $\alpha$ -ethyl naphthalene in the table below.

	Boiling point	Specific gravity	Refractive index	Picrate m.p.
$\alpha$ -vinyl naphthalene	126-129°C (18 mm)	$d_4^{20}$ 1.034	$n_D^{20}$ 1.6436	101-102°C
$\alpha$ -ethyl naphthalene	257-259.5°C	$d_4^{20}$ 1.0111	$n_D^{20}$ 1.6089	98-98.5
Dehydrogenated product	250-255°C	$d_4^{25}$ 1.0248	$n_D^{25}$ 1.6022	98

Dehydrogenation with sulfur. A mixture of 12 g. of tetraallyl ethyl alcohol and 4.8 g. of sulfur was heated for 4 hours. The reaction was carried out at 180-190°C, the temperature being raised to 210-215°C only during the last hour. The viscous, dark brown mixture was then distilled in vacuum. We obtained 7.8 g. (66.22% of theoretical) of a yellowish liquid with a b.p. of 152-154°C at 4-5 mm ( $\beta$ -naphthyl ethanol). A considerable quantity of viscous black material remained in the flask.

In accordance with the prescriptions of Newman<sup>[9]</sup> the naphthyl ethanol was converted to the bromide with a b.p. of 188-189°C at 25 mm.  $\beta$ -(1-naphthyl)-ethyl malonate, which distills over at 213-215°C at 7 mm, was prepared by the condensation of the bromide with sodium malonic ester<sup>[10]</sup>.

$\beta$ -(1-naphthyl)-ethyl-(3-chlorocrotyl)-malonic ester (LII). 30 g. of freshly distilled 1,3-dichlorobutene-2 were gradually added to a solution of the sodium derivative of  $\beta$ -(1-naphthyl)-ethyl malonate, prepared from 58.1 g. of the ester, 4.6 g. of sodium, and 46 g. of absolute alcohol, with constant stirring and water cooling. After standing for half an hour at room temperature, the mixture was thoroughly boiled, with a reflux condenser, for 5 hours, after which much of the alcohol was driven off. To the residue there was added an amount of water acidulated with hydrochloric acid sufficient to dissolve the salt formed. The reaction product was dissolved in benzene, the benzene solution being washed with water and dried with anhydrous sodium sulfate. After the solvent had been driven off, the residue was distilled in vacuum. We obtained 68.67 g. (88.00 % of theoretical) of a viscous oil boiling at 243-244°C at 4 mm:



$d_{40}^{20}$  1.1298;  $n_D^{20}$  1.5390;  
 0.1322 g. substance: 0.0482 AgCl.  
 0.1094 g. substance: 0.0390 AgCl.  
 Found %: Cl 9.02, 8.82.  
 $C_{23}H_{17}O_4Cl$ . Calculated %: Cl 8.82.

$\beta$ -(1-naphthyl)-ethyl-(3-chloroacetyl)-malonic acid (IV). A mixture of 65 g. of the ester (III), 19 g. of caustic soda, and 260 g. of 95% alcohol was boiled with a reflux condenser for 4 hours, after which 150 ml. of water was added and the alcohol entirely driven off. After acidulation with a chilled solution of hydrochloric acid, a heavy oil separated out, which crystallized upon standing. This substance was dissolved in ether, and the ether solution was washed with water and dried with anhydrous sodium sulfate. The crystalline substance that remained after the ether had been driven off was recrystallized from a mixture of acetone and benzene. We obtained 41.8 g. (55.95% of theoretical) of colorless small crystals with a m.p. of 168.5-169°C. The acid (IV) is easily soluble in ether and acetone, but very poorly soluble in benzene.

0.1244 g. substance: 0.0522 g. AgCl.  
 0.1148 g. substance: 0.0476 g. AgCl.  
 Found %: Cl 10.38; 10.27.  
 $C_{19}H_{15}O_4Cl$ . Calculated %: Cl 10.25.

$\alpha$ -(3-chloroacetyl)- $\gamma$ -(1-naphthyl)-butyric acid (II). 38.5 g. of the pure dibasic acid (IV) were decomposed by heating over an open flame. The thick oil remaining in the flask was dissolved in benzene; after the latter had been driven off, the oil crystallized almost completely. The uncrystallized oil was squeezed out of the crystals, which were then recrystallized from dilute alcohol. We obtained 24.42 g. (72.65% of the theoretical value) of a colorless, fine-crystalline powder with a m.p. of 86-87°C.

0.1174 g. substance: 0.0568 g. AgCl.  
 0.1012 g. substance: 0.0490 g. AgCl.  
 Found %: Cl 11.96, 11.97.  
 $C_{18}H_{13}O_2Cl$ . Calculated %: Cl 11.73.

3-keto-1,2,3,11,12,12a-hexahydrochrysene (I). To 180 g. of 84.5% sulfuric acid 9 g. of the acid (II) are gradually added at room temperature. As the latter was added, the mixture turned more and more intensively yellow. After the mixture had been heated on a water bath in a current of carbon dioxide, hydrogen chloride began to be liberated abundantly. The temperature of the bath was kept at 60-65°C for an hour and a half until the substance had been fully dissolved and no more hydrogen chloride was liberated, after which the dark red solution was allowed to stand overnight. The next day the contents of the flask were decanted over ice, the crystalline substance that separated out being dissolved in benzene, and the benzene solution carefully washed with a potash solution and then with water, and dried with anhydrous sodium sulfate. After the benzene had been driven off, there remained 5.8 g. (78.61% of theoretical) of a yellowish substance. The colorless substance obtained by double recrystallization from benzene and alcohol fused at 187-187.5°C (Wilds and Shunk [4] give the m.p. as 188-188.5°C). The substance dissolves easily in benzene, but is hardly soluble at all in alcohol or ether.

0.1002 g. substance: 0.3218 CO<sub>2</sub>; 0.0636 g. H<sub>2</sub>O.  
 Found %: C 87.52, H 6.98.  
 $C_{29}H_{26}O$ . Calculated %: C 87.1; H 6.7.

A mixture of 1.5 g. of the ketone, 1.5 g. of barium carbonate, 1 g. of hydroxylamine hydrochloride, and 40 ml. of alcohol was boiled over a water bath for 8 hours, after which it was filtered while hot. A large part of the pyridine was removed by alternately adding alcohol and partially driving it off from the solution. The oxime that settled out of the solution upon chilling was filtered, washed with alcohol and water, and recrystallized from a mixture of alcohol and benzene. Small, cream-colored crystals, melting with decomposition at 216°C (Wilds and Shunk [4] give the m.p. as 219-222°C), were obtained. Repeated crystallization did not change the melting point of the oxime.

5.370 mg. substance: 0.233 ml  $N_2$  (21°C, 738 mm).  
Found %: N 4.89.  
 $C_{18}H_{17}ON$ . Calculated %: N 5.32.

#### CONCLUSIONS

1.  $\alpha$ -(3-chlorocrotyl)- $\gamma$ -(1-naphthyl)-butyric acid (II) has been prepared from  $\beta$ -(1-naphthyl)-ethyl bromide and 1,3-dichlorobutane-2 by means of malonic-ester synthesis.
2. By sulfuric acid hydrolysis and double cyclization of the acid (II) 3-keto-1,2,3-, 11,12,12a-hexahydrochrysene (I) has been prepared.
3. It has been demonstrated that the method of preparing ketones of the phenanthrene series developed previously can be employed in the preparation of ketones of the cyclic system of chrysene.

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## ALKYLATION OF BENZENE IN THE PRESENCE OF $\text{HSO}_4\text{AlCl}_2$

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Among the numerous mixed and composite catalysts employed in the alkylation of aromatic compounds the compound  $\text{HSO}_4\text{AlCl}_2$  is of considerable interest.

A compound of the residues of sulfuric acid and aluminum chloride, known for its remarkable alkylating ability, orienting influence, and degree of isomerization of radicals, this substance ought to possess a number of specific characteristics. In some degree it may repeat the properties of one or another of its constituents, but may also prove to be a completely singular catalyst. This singularity may appear principally in its selective activity with respect to various compounds, as well as in its orienting and isomerizing ability. This catalyst is mentioned in the patent issued to Schmerling and Rpatieff [1], who proposed its use in alkylation, polymerization, and isomerization.

We investigated the alkylation of benzene with the olefins, halogen derivatives, and alcohols.

The catalyst was prepared by the reaction:



from a mixture of equimolecular quantities of  $\text{AlCl}_3$  and  $\text{H}_2\text{SO}_4$ ; heating the mixture to  $120^\circ\text{C}$  until no more hydrogen chloride is liberated. The substance prepared in this fashion is apparently not a single compound. The possibility of other substances being present is indicated by the fact that when  $\text{H}_2\text{SO}_4$  acts upon  $\text{AlCl}_3$ , a little more than one weight equivalent of hydrogen sulfide is liberated. Owing to its slight hygroscopicity  $\text{HSO}_4\text{AlCl}_2$  is easier to handle than aluminum chloride. The catalyst often loses its activity in storage.

The condensation of benzene with the olefins (pseudobutylene, amylene) requires 0.3 - 0.6 moles of catalyst per mole of the olefin (in each case an excess of benzene is used). The optimum conditions for performing these reactions are: the reagents are added at  $0^\circ\text{C}$ , the mixture is allowed to stand for a long time at  $10-12^\circ\text{C}$ , and then it is heated for a short time at  $20-30^\circ\text{C}$ . The output of alkyl benzenes thereby is 84-86% of theoretical. During the reaction a liquid complex is formed.

The condensation of halogen derivatives ( $n\text{-C}_4\text{H}_9\text{Cl}$  and  $\text{iso-C}_4\text{H}_9\text{Cl}$ ) with benzene in the presence of  $\text{HSO}_4\text{AlCl}_2$  requires somewhat tougher conditions than the corresponding reaction in the presence of  $\text{AlCl}_3$ . With  $\text{AlCl}_3$  reactions of this sort take place at as low as  $-20^\circ\text{C}$ ; with  $\text{HSO}_4\text{AlCl}_2$  the mixture has to be heated over a water bath for several hours. For the condensation of  $\text{iso-C}_4\text{H}_9\text{Cl}$ , 0.07 mole of the catalyst was found to be sufficient; the yield of alkylation products was 60% of theoretical; the alkylation of  $n$ -butyl chloride requires a larger amount of catalyst: 0.11 mole; the yield of alkyl products is 77% of theoretical. When the quantity of catalyst is increased to 0.5 mole, the overall yield rises to 83%, but the output of monobutylbenzene drops from 73 to 66.5%. The reaction is accompanied by the formation of a red-brown complex.

The reaction with alcohols was investigated with the primary ( $n\text{-C}_4\text{H}_9\text{OH}$ ), iso-primary ( $\text{iso-C}_4\text{H}_9\text{OH}$ ), secondary ( $\text{iso-C}_6\text{H}_7\text{OH}$ ), and tertiary ( $\text{tert-C}_5\text{H}_{11}\text{OH}$ ) alcohols. This was necessary

because the influence of the structure of the alcohol radical [2] makes itself felt with particular severity in the alkylation reactions of alcohols. Under our conditions the primary alcohols did not enter into the reaction at all, isopropyl alcohol yielded 5%, and tert-amyl alcohol yielded 50% of alkylation products.

When we compare these results with the figures for the alkylation of benzene by corresponding substances in the presence of  $\text{AlCl}_3$  [3] and  $\text{H}_2\text{SO}_4$  [4], we note the following. In reactions with olefins,  $\text{HSO}_4\text{AlCl}_2$  has an advantage over  $\text{AlCl}_3$  and  $\text{H}_2\text{SO}_4$ , as it yields somewhat higher yields of the alkyl benzenes, and the reaction is not accompanied by side reactions -- polymerization of the olefins and sulfonation of the aromatic hydrocarbons. In reactions with halogen derivatives the same quantity of catalyst is required as when  $\text{AlCl}_3$  is used, but the temperature must be somewhat higher. This must not be considered a major defect of the catalyst however, as the reaction temperature is easily attainable. Compared to  $\text{H}_2\text{SO}_4$ , the new catalyst has considerable advantages, since the alkylation of halogen derivatives in the presence of  $\text{H}_2\text{SO}_4$  is not too successful. In reactions with alcohols  $\text{HSO}_4\text{AlCl}_2$  is not very active; the reaction is appreciable only with the tertiary alcohols, which is due, apparently, to their prior dehydration. In this respect all the advantages lie with  $\text{AlCl}_3$  and  $\text{H}_2\text{SO}_4$ .

In the process of alkylation in the presence of  $\text{HSO}_4\text{AlCl}_2$  the radical is often isomerized. When a second group enters, para isomers are formed; meta isomers were not found. When a third group enters, 1,3,5-isomers are formed; this is apparently due to the isomerization of the 1,2,4-isomers initially formed.

These facts indicate that  $\text{HSO}_4\text{AlCl}_2$  differs considerably from  $\text{AlCl}_3$  as well as from  $\text{H}_2\text{SO}_4$ . A characteristic of this catalyst is its slight activity with alcohols. As for the structure of the catalyst, of the two possible forms: the open  $\text{AlCl}_2\text{OSO}_2\text{OH}$  and the complex  $(\text{AlCl}_2\text{SO}_4)\text{H}$ , the latter seems to us to be the more probable.

#### EXPERIMENTAL

##### Condensation of Benzene with Olefins

The reaction was effected in a three-necked flask with a mechanical stirrer, a reflux condenser with a calcium chloride tube, and two Tishchenko flasks -- one with water the other with bromine water. The benzene and the catalyst were placed in the flask; a chilled solution of the olefin in benzene was introduced through the second neck of the flask by means of a dropping funnel connected to another reflux condenser. In some experiments the catalyst was introduced through this neck together with the benzene olefin mixture. A thermometer was inserted in the third neck of the bottle. To prevent loss of the olefin the reaction was carried out at  $0^\circ\text{C}$ ; the mass was then allowed to stand for several hours (12-20 hours) at room temperature; and finally it was heated to  $20-30^\circ\text{C}$  for, say, an hour. The reaction was accompanied by the formation of an orange-red complex and the liberation of  $\text{HCl}$ . In some experiments the bromine water sometimes bleached out. Further treatment followed customary lines.

Pseudobutylene--benzene. a) Used:  $\text{C}_4\text{H}_8$  -- 13.7 g (0.24 mole); benzene -- 58 g (0.74 mole); catalyst -- 14.4 g (0.075 mole).

The pseudobutylene was added to the mixture of the catalyst and benzene. Product: butylbenzene fraction with b.p. of  $150-205^\circ\text{C}$ : 16.9 g (51.4%); fraction with b.p. of  $205-320^\circ\text{C}$ : 8.2 g. (35% in terms of dibutylbenzene).

b) Used:  $\text{C}_4\text{H}_8$  -- 13.9 g. (0.25 mole); benzene -- 54 g. (0.72 mole); catalyst -- 28.8 g (0.15 mole).

The catalyst was added to a mixture of pseudobutylene and benzene. Product: butylbenzene fraction with a b.p. of  $150-205^\circ\text{C}$  21.8 g. (65%); fraction with b.p. of  $205-320^\circ\text{C}$ : 4.6 g. (19.4%). Redistillation over sodium yielded the following hydrocarbons:

1) Secondary butylbenzene, b.p.  $171-173^\circ\text{C}$ ;  $d_4^{20}$  0.8631;  $n_D^{18}$  1.4885;  $M_D$  44.77; Calcul.  $M_D$  44.78. Acetamide derivative, m.p.  $128^\circ\text{C}$ ; diacetamide derivative, m.p. 185 . . .

\* Here and henceforth the boiling point is stated for 730 mm.



2) n-di-sec.-butylbenzene, b.p. 230-240°C,  $d_4^{20}$  0.8612;  $n_D^{20}$  1.4889;  $MR_D$  63.66. Calculated:  $MR_D$  63.23. When the hydrocarbon was oxidized by 15%  $HNO_3$  in a sealed tube at 135°C, we obtained terephthalic acid; the latter's dimethyl ester had a m.p. of 140°C.

3) 1,3,5-tri-sec.-butylbenzene, b.p. 154-160°C (12 mm);  $d_4^{20}$  0.8719;  $n_D^{20}$  1.5103. When oxidized with dilute  $HNO_3$  we obtained trimesic acid, with a m.p. of 325°C; its trimethyl ester (unpurified) had a m.p. of 134°C (m.p. of the pure ester is 143°C).

None of these hydrocarbons gave the reaction for double bonds. The intermediate fractions bleached a solution of  $KMnO_4$ ; their iodine numbers (by the Hübel method) were determined and found to be 4 -- 12 for the various fractions. These figures indicate that the pseudobutylene contained negligible percentages of polymers.

**Amylene-benzene.** Amylene was prepared by the dehydration of the isoamyl alcohol of fermentation [5] with a b.p. 32-42°C. Used:  $C_5H_{12}O$  - 20 g (0.29 mole); benzene - 70 g (0.9 mole); catalyst - 14.3 g. (0.075 mole). A solution of amylene in benzene was added to a mixture of benzene and the catalyst. Product: amylbenzene fraction with a b.p. of 175-210°C: 17.8 g (42%); diamylbenzene fraction with a b.p. of 210-280°C: 6.8 g. (21.8%). The following were isolated by secondary distillation over sodium:

Amylbenzene, b.p. 184-188°C  $d_4^{20}$  0.8781;  $n_D^{20}$  1.4968;  $MR_D$  49.31. Calculated:  $MR_D$  49.40;

Diamylbenzene, b.p. 255-270°C;  $d_4^{20}$  0.9019;  $n_D^{20}$  1.4780.

#### Condensation of Benzene with Halogen Derivatives

The reaction was effected in the usual vessel without a stirrer; the halogen derivative was added at room temperature to the mixture of benzene and the catalyst. The reaction was accompanied by the abundant liberation of HCl and the formation of a reddish-brown complex. The reaction was concluded by heating the mixture on a water bath until no more HCl was liberated (8-10 hours). The evolution of much heat accompanied the decomposition of the complex.

**N-butylchloride - benzene.** Used:  $C_4H_9Cl$  -- 13.9 g (0.15 mole); benzene -- 35 g. (0.45 mole); catalyst -- 3.3 g. (0.017 mole). Product: butylbenzene fraction with a b.p. of 140-186°C: 15 g. (74%); 186-250°C fraction: 0.5 g. (3.5%).

Increasing the amount of catalyst fourfold yields an output of these fractions corresponding to 66.5% and 16.5% of the theoretical, respectively. The following fractions were isolated by redistillation over sodium:

1) b.p. 171-175°C;  $d_4^{22}$  0.8580;  $n_D^{22}$  1.4865;  $MR_D$  44.01.  
 $C_{10}H_{14}F_3$ . Calculated:  $MR_D$  44.78.

Monoacetamide derivative, m.p. 121°C.

2) b.p. 175-184°C;  $d_4^{21}$  0.8584;  $n_D^{21}$  1.4889;  $MR_D$  45.04  
 $C_{10}H_{14}F_3$ . Calculated:  $MR_D$  44.78.

Before purification the monoacetamide derivative fused at 107°C; after repeated recrystallizations from water and alcohol the m.p. was 120-121°C. After repeated recrystallizations the m.p. of the diacetamide derivative was 214°C.

These fractions are a mixture of the normal and secondary butylbenzenes, the isomeric product predominating in the first fraction, and the normal in the second.

**Isobutyl chloride - benzene.** Used: iso- $C_4H_9Cl$  - 23 g. (0.25 mole); benzene -- 57.5 g. (0.74 mole); catalyst - 3.3 g. (0.017 mole). Product: butylbenzene fraction with a b.p. of 160-210°C (60%). The following fractions were isolated by redistillation over sodium:

1) B.p. 165-166.5°C;  $d_4^{25}$  0.8594;  $n_D^{25}$  1.4885;  $MR_D$  44.95.  
 $C_{10}H_{14}F_3$ . Calculated:  $MR_D$  44.78.

Acetamide derivative, m.p. 161-162°C.

2) B.p. 166.5-169°C;  $d_4^{20}$  0.8616;  $n_D^{20}$  1.4900;  $MR_D$  44.97.  
 $C_{10}H_{14}F_3$ . Calculated:  $MR_D$  44.78.

Acetamide derivative, m.p. 158-160°C.

Both of these fractions are tertiary butylbenzenes with traces of isobutylbenzene.

#### Condensation of Benzene with Alcohols.

The reaction was carried out in an ordinary vessel without a stirrer. The pulverized catalyst was added in small portions to a mixture of benzene and alcohol, the whole being agitated. After all the catalyst had been added, the mixture was allowed to stand at room temperature for 24 hours, after which it was heated on a water bath until no more HCl was liberated. Further treatment was the standard procedure.

n-Butyl alcohol -- benzene. Used: n- $C_4H_9OH$  -- 34 g. (0.46 mole); benzene -- 53 g. (0.68 mole); catalyst -- 111.6 g. (0.57 mole). About 2 g. of product were obtained with a b.p. of 100-145°C. No reaction took place.

Isobutyl alcohol -- benzene. Used: iso- $C_4H_9OH$  -- 19.5 g. (0.25 mole); benzene -- 44 g. (0.56 mole); catalyst -- 72 g. (0.38 mole). About 1 g. of a fraction with a b.p. of 100-130°C was obtained. No reaction took place.

Isopropyl alcohol -- benzene. Used: iso- $C_3H_7OH$  -- 18.0 g. (0.3 mole); benzene -- 78 g. (1 mole); catalyst -- 37.2 g. (0.2 mole). 1.8 g. (5%) of a fraction with a b.p. of 130-160°C was obtained. Redistillation over sodium yielded isopropylbenzene:

B.p. 149-151°C;  $d_4^{20}$  0.8504;  $n_D^{20}$  1.4845;  $MR_D$  40.40.  
 $C_9H_{12}F_3$ . Calculated:  $MR_D$  40.16.

Tertiary amyl alcohol -- benzene. Used: tert.- $C_5H_{11}OH$  -- 17 g. (0.19 mole); benzene -- 62 g. (0.8 mole); catalyst -- 17.6 g. (0.09 mole). Product 8.4 g. (29.5%) of a fraction with a b.p. of 180-220°C; 4.4 g. (20.5%) of a fraction with a b.p. of 220-310°C. Redistillation over sodium isolated:

Tertiary amylbenzene b.p. 189-192°C;  $d_4^{21}$  0.8634;  $n_D^{21}$  1.4870;  $MR_D$  49.30.  
 $C_{11}H_{16}F_3$ . Calculated  $MR_D$  49.40.

Tertiary diamylbenzene b.p. 260-270°C;  $d_4^{21}$  0.8726;  $n_D^{21}$  1.4870;  $MR_D$  71.30.  
 $C_{15}H_{22}F_3$ . Calculated  $MR_D$  72.49.

Oxidation with 10%  $HNO_3$  in a sealed tube at 150°C yielded terephthalic acid, the dimethyl ester of which had a m.p. of 140°C. No isophthalic acid was found.

#### CONCLUSIONS

1. The alkylation of benzene with olefins, halogen derivatives and alcohols in the presence of  $HSO_4AlCl_2$ .

2. It was demonstrated that condensation with the olefins (yield of alkylation products 78-86% of theoretical) and with the halogen derivatives (yield 60-83% of theoretical) is satisfactory. The reaction with the alcohols is unsatisfactory; primary alcohols are not alkylated, while the secondary alcohols are only slightly alkylated (5% yield), and the tertiary alcohols yield a 50% output of alkyl benzenes.

3. Para isomers are formed during alkylation in the presence of  $HSO_4AlCl_2$ .

4.  $HSO_4AlCl_2$  causes partial isomerization of radicals.

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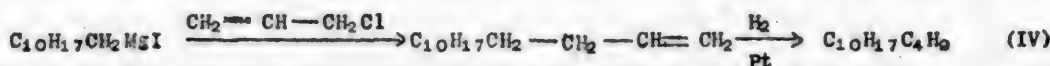
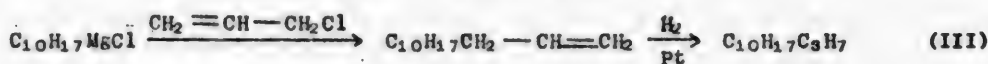
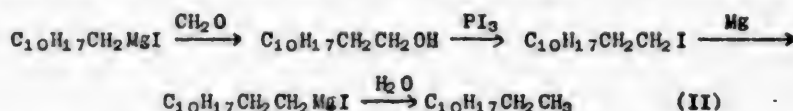
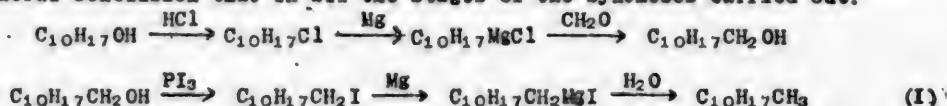
# RESEARCHES IN THE DECALIN SERIES

## IV. BETA METHYL CIS DECALIN

R. Y. Levina, S. G. Kulikov, and Y. A. Bedov

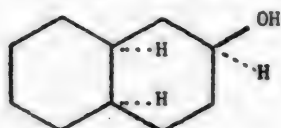
Zelinsky Laboratory of Organic Chemistry of the University of Moscow.

In our previous communications [1] we described the synthesis of four homologs of *cis* and *trans* decalin:  $\beta$ -methyl,  $\beta$ -ethyl,  $\beta$ -propyl, and  $\beta$ -butyl decalins. Comparison of the physical properties of the *cis* and *trans* forms of each hydrocarbon made it possible to draw the general conclusion that in all the stages of the syntheses carried out:



employing in the main the Grignard reaction, the conversion of one stereoisomeric form into the other (*cis*  $\rightleftharpoons$  *trans*) does not occur.

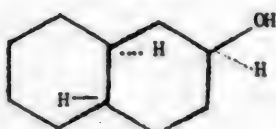
Since the initial substances in these syntheses are the *cis* and *trans* decalols with definite configurations of the asymmetrical  $\beta$ -carbon atom of the decalin ring, we may consider that the hydrocarbons prepared likewise possess this configuration



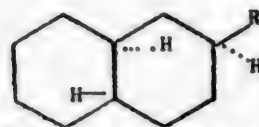
$\beta$ -*cis* decalol  
m.p. 105°C



$\beta$  alkyl *cis* decalin

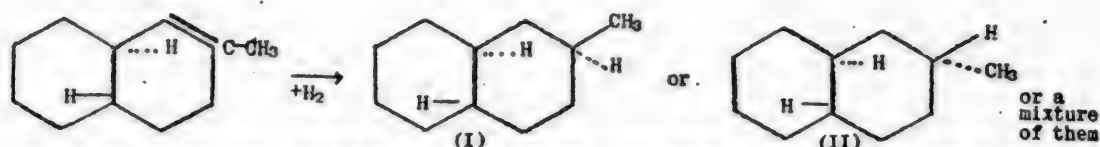


$\beta$  *trans* decalol  
m.p. 75°C



$\beta$  alkyl *trans* decalin

Ruzicka, Koolhaus, and Wind [2] employed the reaction of  $\beta$ -methyl trans decalin with methyl magnesium iodide as the first stage of the synthesis of  $\beta$ -methyl trans decalone. The  $\beta$ -methyl trans decalol prepared was then dehydrated, forming  $\beta$ -methyl trans octalin; subsequent hydrogenation yielded  $\beta$ -methyl trans decalin. Inasmuch as the formation of the asymmetrical  $\beta$ -carbon atom of the ring took place during the hydrogenation of the double bond, it is hard to say which of the racemic stereoisomeric forms of  $\beta$ -methyl trans decalin is obtained as a result of the entire synthesis:



The constants of the hydrocarbon prepared by the authors cited were found to be rather close to the constants of  $\beta$ -methyl trans decalin synthesized by us earlier by another method [3] (cf the diagram given above) and apparently possessing structure (I) corresponding to the structure of the initial  $\beta$ -decalog with a m.p. of 75°C (Table I).

Table I

$\beta$ methyl trans decalin	b.p.	$n_D^{20}$	$d_4^{20}$	$M_R^D$		$EM^D$	Author
				Found	computed		
From $\beta$ trans decalone	76°C (12 mm)	1.4681	0.8670	48.75	48.60	+0.15	Ruzicka et al [2]
From $\beta$ trans decalol with m.p. of 75°C	76°C (12 mm)	1.4698	0.8693	48.85	48.60	+0.25	Levina and Kulikov [3]

It would be of interest to compare the constants of two preparations of  $\beta$  methyl cis decalin obtained by different methods: from beta cis decalol with a m.p. of 105°C by reactions described in our second communication [9] (cf. diagram above), and from  $\beta$  cis decalone by the reactions described in the paper by Ruzicka and his associates for the trans isomer. In the present paper we present experimental data on the synthesis of  $\beta$  methyl cis decalin from  $\beta$  cis decalone.

#### EXPERIMENTAL

##### 1. Preparation of $\beta$ Cis Decalone

An aqueous solution of chromic anhydride (41 g.  $CrO_3$  in 100 ml. water) was gradually added to 82 g. of  $\beta$  cis decalol with a m.p. of 105°C, with constant agitation by a stirrer. The reaction mixture was allowed to stand overnight. The ketone formed was driven out of the reaction mixture by steam and then extracted with ether. After the ether had been driven off from the washed and dried extract, the ketone was distilled with a Vigret dephlegmator. Yield: 53% of theoretical.

B.p. 249.8-250.3°C (746 mm);  $n_D^{21}$  1.4918;  $d_4^{21}$  1.0039;  $M_R^D$  43.95.

$C_{10}H_{16}O$ . Calculated  $M_R^D$  43.99.

Literature data: Huckel and Mentzel

B.p. 248°C (760 mm);  $n_D^{20}$  1.4918;  $d_4^{20}$  1.003;  $M_R^D$  43.99.

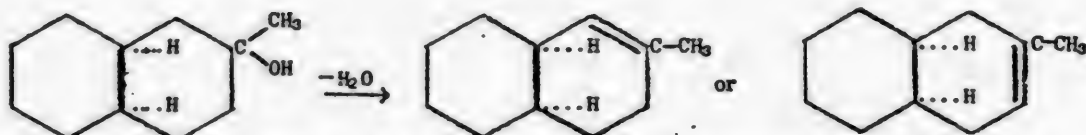
##### 2. Preparation of $\beta$ -Methyl- $\beta$ -Cis Decalol.

The reaction of  $\beta$  cis decalone (40 g) with methyl magnesium iodide (97 g.  $CH_3I$  and 16.5 g. Mg) was effected under the usual Grignard reaction conditions. The reaction mixture was heated over a water bath for 4 hours. Decomposition was effected by dilute acetic acid. After



the ether had been driven off from the washed and dried ether extract, and the reaction product had been twice fractionated in vacuum (with a Vigret dephlegmator),  $\beta$ -methyl- $\beta$ -cis decalol (14 g., or 32% of theoretical) was isolated in the form of an extremely viscous liquid with a b.p. of 122-122.5°C (12 mm) and an  $n_D^{20}$  of 1.4985.  $\beta$ -methyl- $\beta$ -cis decalol is not described in the literature.

### 3. Preparation of $\beta$ Methyl Cis Octalin



The dehydration of  $\beta$  methyl  $\beta$ -cis decalol (22.6 g.) was effected by heating it with 97% formic acid (45 g.). After heating it for six hours on a boiling water bath, the top layer of the reaction mixture was removed, washed until it exhibited a neutral reaction, dried with sodium sulfate, and distilled twice over metallic sodium (with a Vigret dephlegmator).  $\beta$ -methyl cis octalin is not described in the literature. The  $\beta$  methyl cis octalin (yield - 10.6 g., or 58% of theoretical) possessed the following constants:

B.p. 85°C (11 mm);  $n_D^{20}$  1.4928;  $d_4^{20}$  0.9056;  $MR_D$  48.00.

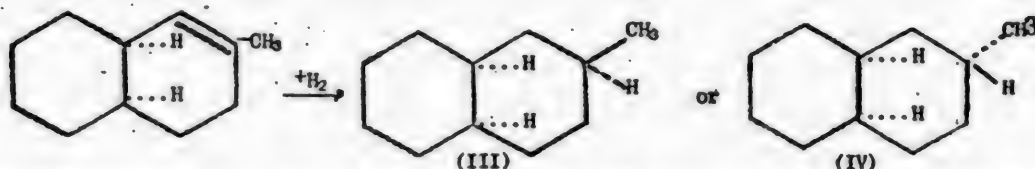
$C_{11}H_{18}$ . Calculated:  $MR_D$  48.13.

0.2050 g. substance : 0.6599 g.  $CO_2$ ; 0.2236 g.  $H_2O$ .

Found %: C 87.79; H 12.12.

$C_{11}H_{18}$ . Calculated %: C 87.93; H 12.07.

### 4. Preparation of $\beta$ Methyl Cis Decalin



The hydrogenation of  $\beta$ -methyl cis octalin (7 g.) was effected in the cold in the presence of a platinized needle in a solution of cyclohexane. Table 2 gives the constants of  $\beta$ -methyl cis decalin prepared (after treatment with 80% sulfuric acid) and, for the sake of comparison, the constants of the same hydrocarbon prepared by us previously [3] by another method (from  $\beta$  cis decalol), by the reactions given in the diagram shown above and apparently pos-

Table II

$\beta$ methyl cis decalins	b.p. at 12 mm	$n_D^{20}$	$d_4^{20}$	$MR_D$		$EM_D$
				Found	computed	
From $\beta$ cis decalone	84-84.5°C	1.4752	0.8815	48.63	48.60	--
From $\beta$ cis decalol (m.p. 105°C)	84	1.4751	0.8846	48.47	48.60	-0.13

sessing structure (III), which corresponds to the structure of the initial beta cis decalol, with a m.p. of 105°C. It is evident from the data in Table 2 that the constants of the  $\beta$ -methyl cis decalin synthesized by us from  $\beta$  cis decalone are quite close to those of the same hydrocarbon synthesized by us earlier [3] from  $\beta$  cis decalol, with a m.p. of 105°C.

The same conclusion may be drawn from the data of Table 1 with regard to the two preparations of  $\beta$  methyl trans decalin synthesized by Ruzicka [2] from  $\beta$  trans decalone and by us [3] from  $\beta$  trans decalol, with a m.p. of 75°C.

Thus, apparently, it may be concluded that both methods of synthesizing the  $\beta$ -alkyl decalins described in the present and in previous communications yield a single racemic form of the two possible cis forms and a single racemic form of the two possible trans forms.

#### CONCLUSIONS

1. The synthesis of  $\beta$  methyl cis decalin in three successive stages is described: the interaction of methyl magnesium iodide and  $\beta$  cis decalone; the dehydration of the tertiary alcohol produced; and the hydrogenation of the methyl cis octalin formed in this reaction.

2. The constants of the  $\beta$  methyl cis decalin prepared were found to be close to the constants of the same hydrocarbon as synthesized by us previously by another method from  $\beta$  cis decalol, with a m.p. of 105°C. and apparently possessing the spatial configuration of the latter.

3. Hence, it may be concluded that both methods of synthesizing  $\beta$  alkyl cis decalins described in our present and previous communications yield a single racemic form of the two possible cis forms.

4.  $\beta$  methyl  $\beta$  cis decalol and  $\beta$  methyl cis octalin are described for the first time.

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# RESEARCH IN THE CHEMISTRY OF ALKYL SULFO ACIDS

## III. PREPARATION OF ARYL AMIDES OF ALKYL SULFO ACIDS

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Some of the aromatic derivatives of the aliphatic sulfamides are known. For instance, not so very long ago the anilide of methane sulfonic acid [1] was described; Glutterbouck and Cohen described the action of aniline on the disulfochloride of ethionic acid [2]; and Latimer and Bost [3] prepared and described the *n*-toluidides and the *n*-phenetidides of methane, ethane, butane, and pentane sulfonic acids, noting that the *n*-toluidides of methane and ethane sulfonic acids possess pharmacological properties -- their action is like that of antipyrine and other antineuralgic remedies. The pharmacological properties of the *n*-phenetidine of ethane sulfonic acid were known at an earlier date [4]. Raudenbusch endeavored to prepare the anilide of  $\alpha$ -chloroethane sulfonic acid, but this effort was unsuccessful [5].

We prepared a series of aryl amides of chloromethane and  $\alpha$ -chloroethane sulfonic acids by means of the action of sulfochlorides (prepared as described earlier [6]) upon the aromatic amines in an ether medium. The substances prepared by us, with the exception of the anilide of  $\alpha$ -chloroethane sulfonic acid, are well-defined crystalline compounds soluble in organic solvents.

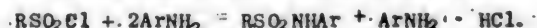
No.	Compound formula	Melting point	Solubility				% Nitrogen	
			Alcohol	Water	Benzene	Ether	Found	computed
I	$\text{CH}_2\text{ClSO}_2\text{NHC}_6\text{H}_5$ .....	69°C	Good	Poor	Good	Good	6.83	6.81
II	$\text{CH}_3\text{CHClSO}_2\text{NHC}_6\text{H}_5$ .....	pasty	Good	Poor	Good	Good	6.38	6.37
III	$\text{CH}_2\text{ClSO}_2\text{NHC}_6\text{H}_4\text{CH}_3$ (o)....	70°C	"	"	"	"	6.00	6.37
IV	$\text{CH}_3\text{CHClSO}_2\text{NHC}_6\text{H}_4\text{CH}_3$ (o) .	52	"	"	"	"	5.90	5.99
V	$\text{CH}_2\text{ClSO}_2\text{NHC}_6\text{H}_4\text{CH}_3$ (p)....	88	"	"	"	"	6.23	6.37
VI	$\text{CH}_3\text{CHClSO}_2\text{NHC}_6\text{H}_4\text{CH}_3$ (p) .	82	"	"	"	"	5.73	5.99
VII	$\text{CH}_2\text{ClSO}_2\text{NHC}_6\text{H}_4\text{CH}_3$ (m) ...	69	"	"	"	"	6.18	6.37
VIII	$\text{CH}_3\text{CHClSO}_2\text{NHC}_6\text{H}_4\text{CH}_3$ (m) ..	92	"	"	"	"	5.86	5.99
IX	$\text{CH}_2\text{ClSO}_2\text{NHC}_6\text{H}_4\text{OC}_2\text{H}_5$ (m) ..	90	"	"	"	"	5.31	5.61
X	$\text{CH}_3\text{CHClSO}_2\text{NHC}_6\text{H}_4\text{OC}_2\text{H}_5$ (m)	65	"	"	"	"	5.16	5.31
XI	$\text{CH}_2\text{ClSO}_2\text{NHC}_6\text{H}_7$ ( $\alpha$ ) .....	120	"	"	"	"	5.51	5.47
XII	$\text{CH}_3\text{CHClSO}_2\text{NHC}_6\text{H}_7$ ( $\alpha$ )....	138	"	"	"	"	4.89	5.19
XIII	$\text{CH}_2\text{ClSO}_2\text{NHC}_6\text{H}_7$ ( $\beta$ ).....	105	"	"	"	"	5.45	5.47
XIV	$\text{CH}_3\text{CHClSO}_2\text{NHC}_6\text{H}_7$ ( $\beta$ )....	115	"	"	"	"	5.00	5.19

The compounds described are of considerable interest from the standpoint of explaining the influence of chlorine within the radical, as well as the influence of the position of the substituents within the aromatic ring (ortho, meta, and para), upon pharmacological properties. The compounds prepared and their basic properties are listed in the table above.

As may be seen from the table, the series of compounds prepared by us exhibits a definite regularity and constancy of properties. Thus, they exhibit identical behavior toward solvents; the melting points of the anilides, toluides, and phenetides of chloromethane sulfonic acid are, as a rule, higher than for the similar derivatives of chloroethane sulfonic acid. The *m*-toluides constitute an exception. The situation is reversed with the naphthylides.

The hydrogen of the NH group has acid characteristics in all the compounds listed in the table, which is why they dissolve in bases. This ability was exploited by us to isolate them from impurities by converting them into an alkaline solution and then separating them from their alkaline solutions by means of acidification.

The formation of aryl amides follows the equation below:



#### EXPERIMENTAL

##### 1. Preparation of the anilide of chloromethane sulfonic acid (I)\*

4.6 g of chloromethane sulfochloride were dissolved in 40 ml of absolute ether. 5.7 g of aniline were added to the solution in small portions; the solution grew cloudy, and a slight amount of heating (25-30°C) was observed. A precipitate of aniline hydrochloride soon deposited out. The reaction mixture was allowed to stand for several hours until the reaction was over. The precipitated salt was filtered out. The ether filtrate was evaporated, leaving as a residue a viscous brown oil, which dissolved in a 5% base. The tarry impurities that did not dissolve in the base were filtered out, while the end product was isolated from the alkaline solution by acidifying the latter with dilute sulfuric acid until the turbidity remained constant. A yellow oil, which upon chilling hardened into a solid crystalline mass, gradually settled on the bottom of the vessel. This was filtered out and purified by dissolving it in a small quantity of alcohol and then precipitating it with water. Yield: 2.8 g. Purification may be effected by recrystallization from water. The dried product melted at 69°C.

0.1828 g. substance: 8.92 ml. 0.1 N.  $\text{H}_2\text{SO}_4$  (Kjeldahl).  
 Found %: N 6.83  
 $\text{C}_7\text{H}_9\text{O}_2\text{NSCl}$ . Calculated %: N 6.81.

##### 2. Preparation of the anilide of $\alpha$ -chloroethane sulfonic acid (II)

We took 20 g of  $\alpha$ -chloroethane sulfochloride in 60 ml of ether and 22.8 g of aniline. The reaction was carried out as before. When the oily product was dissolved in the base and then precipitated with sulfuric acid, it did not crystallize. The oil was reconverted to an ether solution. After the ether had been evaporated we again obtained a yellow oil. Yield: 8.5 g. An oily substance continued to separate out after purification from water as well as from water and alcohol. When this substance was distilled in vacuum, the bulk of it decomposed at 196°C and 5 mm, only a quite negligible portion distilling over as a transparent liquid, which soon congealed into a waxy yellow mass. In determining the melting point of this substance it began to fuse at 27°C, but did not turn transparent, not even at higher temperatures of from 80 to 100°C. The anilide that is not distilled in vacuum likewise congeals into a waxy mass upon prolonged standing in the cold. We were unable to obtain well-defined crystals from this mass. The density of the oil was not determined owing to its high viscosity.

0.2060 g. substance: 9.4 ml. 0.1 N.  $\text{H}_2\text{SO}_4$   
 Found %: N 6.38.  
 $\text{C}_8\text{H}_{10}\text{O}_2\text{NSCl}$ . Calculated %: N 6.37.

##### 3. Preparation of the *o*-toluide of chloromethane sulfonic acid (III)

We took 5.3 g of the chloride in 50 ml of ether and 7.6 g. *o*-toluidine. The oily reaction product crystallized only after long standing. Yield: 2 g. It was purified by recrystallization from water: *m p.* 70°C.

\* The method of preparation is described for the first two compounds. The others were prepared by the same method.



0.2968 g substance: 12.72 ml. 0.1 N.  $\text{H}_2\text{SO}_4$   
Found %: N 6.00.  
 $\text{C}_8\text{H}_{10}\text{O}_2\text{NSCl}$ . Calculated %: N 6.37.

4. Preparation of the o-toluide of  $\alpha$ -chloroethane sulfonic acid (IV).

We took 4.56 g of the chloride in 50 ml. of ether and 6 g. of ortho toluidine. The oily reaction product crystallized only after long standing. Yield: 1.5 g. The substance recrystallized from water fused at  $52^\circ\text{C}$ .

0.1232 g substance: 5.25 ml 0.1 N.  $\text{H}_2\text{SO}_4$   
Found %: N 5.96  
 $\text{C}_9\text{H}_{12}\text{O}_2\text{NSCl}$ . Calculated %: N 5.99.

5. Preparation of the p-toluide of chloromethane sulfonic acid (V).

We took 6.9 g of the chloride in 60 ml of ether and 9.9 g of p-toluidine. Yield of product: 3 g. It was recrystallized from water; m.p.  $88^\circ\text{C}$ .

0.0478 g substance: 2.136 ml 0.1 N.  $\text{H}_2\text{SO}_4$   
Found %: N 6.23.  
 $\text{C}_9\text{H}_{10}\text{O}_2\text{NSCl}$ . Calculated %: N 6.37.

6. Preparation of the p-toluide of  $\alpha$ -chloroethane sulfonic acid (VI).

We took 3.8 g of the chloride in 50 ml of ether and 5 g of p-toluidine. Yield of product: 2.9 g. It was recrystallized from water; m.p.  $82^\circ\text{C}$ .

0.2002 g substance: 8.2 ml 0.1 N.  $\text{H}_2\text{SO}_4$   
Found %: N 5.73.  
 $\text{C}_9\text{H}_{12}\text{O}_2\text{NSCl}$ . Calculated %: N 5.99.

7. Preparation of the m-toluide of chloromethane sulfonic acid (VII).

We took 2.8 g of the chloride in 40 ml of ether and 4 g of m-toluidine. Yield: 1.4 g. The product was recrystallized from alcohol and water; m.p.  $69^\circ\text{C}$ .

0.1201 g substance: 5.3 ml 0.1 N.  $\text{H}_2\text{SO}_4$   
Found %: N 6.17  
 $\text{C}_8\text{H}_{10}\text{O}_2\text{NSCl}$ . Calculated %: N 6.37.

8. Preparation of the m-toluide of  $\alpha$ -chloroethane sulfonic acid (VIII)

We took 4.91 g of the chloride in 50 ml of ether and 6.4 g m-toluidine. Yield: 4.12 g. Recrystallized from water; m.p.  $92^\circ\text{C}$ .

0.1015 g substance: 4.25 ml. 0.1 N.  $\text{H}_2\text{SO}_4$   
Found %: N 5.86.  
 $\text{C}_9\text{H}_{12}\text{O}_2\text{NSCl}$ . Calculated %: N 5.99.

9. Preparation of the m-phenetide of chloromethane sulfonic acid (IX)

We took 2.95 g of the chloride in 40 ml of ether and 5.4 g of meta phenetidine. Yield: 1.5 g. Recrystallized from water and alcohol; m.p.  $90^\circ\text{C}$ .

0.1762 g substance: 6.7 ml 0.1 N.  $\text{H}_2\text{SO}_4$   
Found %: N 5.32.  
 $\text{C}_9\text{H}_{12}\text{O}_3\text{NSCl}$ . Calculated %: N 5.61.

10. Preparation of the m-phenetide of  $\alpha$ -chloroethane sulfonic acid (X).

We took 2 g of the chloride in 40 ml of ether and 3.4 g of m-phenetidine. Yield: 1 g. Recrystallized from alcohol and water; m.p.  $65^\circ\text{C}$ .

0.1080 g substance: 3.98 ml 0.1 N.  $\text{H}_2\text{SO}_4$   
Found %: N 5.15.  
 $\text{C}_{10}\text{H}_{14}\text{O}_3\text{NSCl}$ . Calculated %: N 5.31.

11. Preparation of the  $\alpha$ -naphthyl amide of chloro-methane sulfonic acid (XI).

We took 4 g of the chloride in 50 ml of ether and 7.6 g of  $\alpha$ -naphthylamine. The salt of  $\alpha$ -naphthylamine that settled out and the reaction product were both colored. Yield of product: 2 g. Purification was effected by dissolving the product in alcohol and heating

slightly with a small quantity of bone black. The bone black was filtered out, and the alcohol solution was diluted with water until it turned cloudy. The  $\alpha$ -naphthyl amide of chloromethane sulfonic acid melts at 120°C. The crystals had a barely perceptible pinkish tinge after triple recrystallization.

0.1106 g substance: 4.36 ml 0.1 N  $H_2SO_4$ .

Found %: N 5.51.

$C_{11}H_{10}O_2NSCl$ . Calculated %: N 5.47.

12. Preparation of the  $\alpha$ -naphthyl amide of  $\alpha$ -chloroethane sulfonic acid (XII).

We took 3.4 g of the chloride in 50 ml of ether and 5.9 g of  $\alpha$ -naphthylamine. The product of the reaction consisted of reddish brown crystals. Yield: 0.4 g. Twofold purification from alcohol and water yielded yellowish-gray crystals with a m.p. of 138°C.

0.1002 g substance: 3.5 ml 0.1 N  $H_2SO_4$ .

Found %: N 4.89.

$C_{12}H_{12}O_2NSCl$ . Calculated %: N 5.19.

13. Preparation of the  $\beta$ -naphthyl amide of chloromethane sulfonic acid (XIII).

We took 4.8 g of  $\beta$ -naphthylamine in 60 ml of ether and added 2.5 g of the sulfochloride in small portions. The reaction product was reddish-yellow. Yield: 1.8 g. It was recrystallized from alcohol (with bone black) and from water. The red, matted crystals had a rosy tinge; m.p. 105°C. Upon a second recrystallization the product became almost colorless.

0.1168 g substance: 4.55 ml 0.1 N  $H_2SO_4$ .

Found %: N 5.45.

$C_{11}H_{10}O_2NSCl$ . Calculated %: N 5.47.

14. Preparation of the  $\beta$ -naphthyl amide of  $\alpha$ -chloroethane sulfonic acid (XIV).

We took 4.7 g of  $\beta$ -naphthylamine in 60 g of ether and 2.7 g of the sulfochloride. The reaction product, after subsidiary treatment with ether, was a reddish, crystalline substance. Yield: 0.2 g. Purified twice from alcohol and from water, it did not lose its coloration. M.p. 115°C.

0.0688 g substance: 2.4 ml 0.1 N  $H_2SO_4$ .

Found %: N 4.88.

$C_{12}H_{12}O_2NECl$ . Calculated %: N 5.19.

CONCLUSIONS

1. The anilides, ortho, meta, and para toluides, the meta phenetides, and the  $\alpha$ - and  $\beta$ -naphthylides of chloromethane and  $\alpha$ -chloroethane sulfonic acids were prepared and described.

2. The compounds prepared, particularly the p-toluides and phenetides, are of pharmacological interest, inasmuch as similar compounds, which do not have chlorine in the radical, however, possess an antineuralgic action.

LITERATURE CITED

- [1] J. Am. Soc., 54, 2470-2476 (1932). — [2] J. Chem. Soc., 121, 120, (1922). — [3] Zbl., I, 3775 (1940). — [4] Huben, T.III., 491. — [5] Raudenbusch. Monograph on the Chlorination of the Trithioacetaldehydes (1928). — [6] Jour. Gen. Chem., (USSR), 11, 63 (1941).

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Dec. 23, 1946.

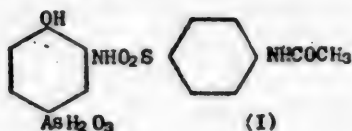
# SULFANILAMIDE COMPOUNDS OF AROMATIC ARSONIUM ACIDS

## II. SULFANILAMIDE DERIVATIVES OF AMINO-3-HYDROXY-4-PHENYLARSINIC ACID

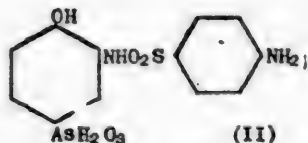
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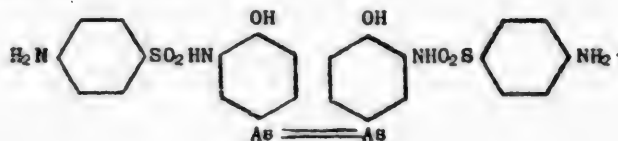
In our previous communication [1] we described the preparation of the sulfanilamide derivatives of p-aminoarsonium acids. At the time we called attention to the therapeutic activity of the synthesized preparations. In connection with the results obtained it seemed to us to be of interest to investigate the sulfanilamide derivatives of amino-hydroxy-phenylarsinic acid. As we know, amino-3-hydroxy-4-phenylarsinic acid is one of the most important raw materials in the production of highly active therapeutic arsenicals. It may be assumed that the sulfanilamide derivatives of this acid might yield interesting results, involving the acquisition of new therapeutic properties. The first sulfanilamide derivative of amino-3-hydroxy-4-phenylarsinic acid is acetosulfanilamido-hydroxy-phenylarsinic acid (I):



We prepared this compound by condensing acetaminobenzene sulfochloride with the sodium salt of amino-3-hydroxy-4-phenylarsinic acid in an aqueous medium. The reaction proceeds smoothly with a good yield at a temperature of 30-40°C. By saponification with hydrochloric acid (sp. gr. 1.097) we prepared aminobenzene-sulfanilamido-hydroxyarsinic acid (II).

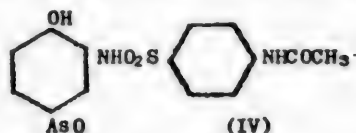


The synthesized compounds were subjected to a reduction reaction. The reduction of acetosulfanilamido-hydroxy-phenylarsinic acid by sodium hydrosulfite is accompanied by the saponification of the acetyl groups, resulting in the formation of an arseno compound (III) of the following composition:

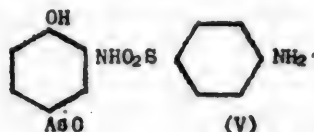


3-3-p-diaminobenzosulfamide-4,4-dihydroxy-arsenobenzene is a colorless substance that melts at 180-182°C (with decomposition). This same substance is likewise obtained by the reduction of aminobenzosulfamido-hydroxyphenylarsinic acid under similar conditions.

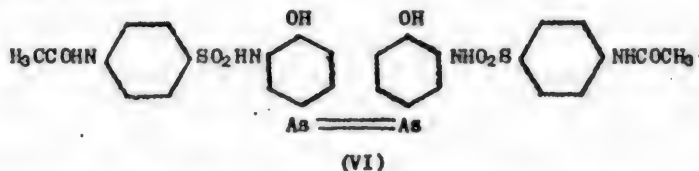
In reducing acetosulfanilamido-hydroxyphenylarsinic acid (I) and aminosulfanilamido-hydroxyphenylarsinic acid (II) with sulfuric acid, we were aiming at the preparation of a substance of composition (IV) by the reduction of the first compound:



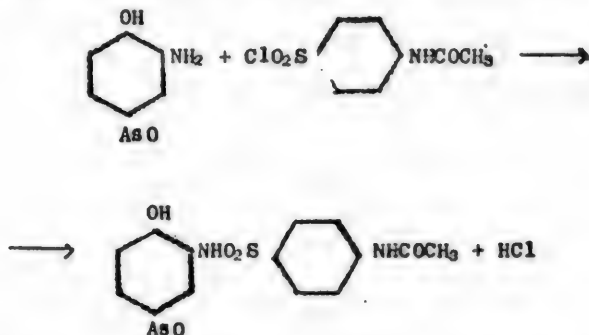
In this case, however, the acetyl group is not preserved. Thus, the reduction of the foregoing compounds (I and II) with sulfuric acid resulted in the formation of the sulfanil-amido-hydroxy-phenylarsenoxide (V):



To prepare 3,3-diacetobenzosulfamide-4,4-dihydroxyarsenobenzene we turned to the reaction of the hydrochloride salt of diamino-3,3-dihydroxy-4,4-arsenobenzene with acetamidobenzene sulfochloride. As a result of this reaction we obtained a compound (VI) corresponding to the following formula:

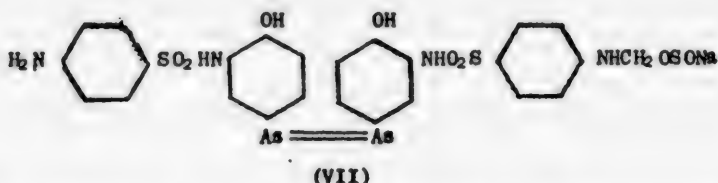


Furthermore, it seemed likely that we could prepare acetosulfanilamido-phenylarsenoxide (V) by the reaction of amino-3-hydroxy-4-phenylarsenoxide with acetamidobenzene sulfochloride:



Preparing amino-3-hydroxy-4-phenylarsenoxide by the method of Ehrlich and Bertheim [2], we carried out the foregoing reaction, but without success. By the action of rongalite upon 3,3-p-diaminobenzosulfamide-4,4-dihydroxy-arsenobenzene we prepared a pale yellow compound of the following composition:





The synthesized compounds were subjected to chemotherapeutical tests. The trypanocidal action of acetosulfanilamido-hydroxyphenylarsinic acid (I) was negligible in doses of 1:150, while the action of aminobenzene-sulfanilamido-hydroxyarsinic acid (II) was very weak with doses of 1:250. 3,3-p-diaminobenzosulfamide-4,4-dihydroxy-arsenobenzene (III) and sulfanilamido-hydroxy-phenylarsin oxide (V) were found to be inactive, the latter also displaying high toxicity. All the preparations were found to be inactive in relapsing fever. In streptococcal infection only 3,3-p-diaminobenzosulfamide-4,4-dihydroxy-arsenobenzene exhibited slight activity. But in experimental pneumonia this preparation, like the others, was completely inactive. 3,3-p-diacetobenzosulfamide-4,4-dihydroxy-arsenobenzene was not tested chemotherapeutically because of its instability and very low solubility.

#### EXPERIMENTAL

##### 1. Reaction of amino-3-hydroxy-4-phenylarsinic acid with acetanilide sulfochloride.

20 g of the freshly prepared sodium salt of amino-3-hydroxy-4-phenylarsinic acid were dissolved in 200 ml of water in a flask equipped with a mechanical stirrer. During the course of 25 minutes acetanilide sulfochloride (20 g), which had been recrystallized from dichloroethane, was gradually added to the salt solution. The reaction lasted half an hour at 30-40° C. After the reaction was over the contents of the flask were filtered. The filtrate was acidified with hydrochloric acid until it was weakly acid with litmus paper. The white precipitate that deposited out upon cooling was filtered out and then washed with water and alcohol. The colorless crystals were insoluble in water, alcohol, acetone, hydrogen sulfide, toluene, carbon tetrachloride, chloroform, ether, benzene, and mineral acids; they were soluble in weak bases. After fourfold purification by reprecipitation and drying in an exsiccator over sulfuric acid, the compound fused at 165-166°C. Yield: 26.2 g.

0.2314 g substance:	10.65 ml N/10 solution of Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> :
0.1900 g substance:	8.75 ml N/10 solution of Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> :
0.2456 g substance:	5.88 ml N/10 solution of NaOH.
4.878 mg substance:	2.690 mg BaSO <sub>4</sub> .
3.728 mg substance:	2.023 mg BaSO <sub>4</sub> .
3.650 mg substance:	5.185 mg CO <sub>2</sub> : 1.240 mg H <sub>2</sub> O.
3.550 mg substance:	5.065 mg CO <sub>2</sub> : 1.195 mg H <sub>2</sub> O.
2.670 mg substance:	0.159 ml N <sub>2</sub> (22°C, 737 mm).
3.779 mg substance:	0.224 ml N <sub>2</sub> (20.5°C, 731 mm).
Found %:	As 17.26, 17.27; (CH <sub>3</sub> CO) 10.26; S 7.57, 7.46;
	C 38.74, 38.90; H 3.80, 3.77; N 6.68, 6.63.
C <sub>14</sub> H <sub>15</sub> N <sub>2</sub> SAO <sub>7</sub> . Calculated %:	As 17.44; (CH <sub>3</sub> CO) 10.0; S 7.44; C 39.10;
	H 3.49; N 6.51.

##### 2. Saponification of acetosulfanilamido-hydroxy-phenylarsinic acid (I).

20 g of the substance and 25 ml of hydrochloric acid (sp. gr. 1.097) were placed in a 250-ml air-cooled round-bottomed flask. The mixture was heated over a boiling water bath for 1 hour 20 minutes. After cooling, the precipitate was filtered out and washed with water and chilled alcohol. The substance was easily soluble in alkalis, but poorly soluble in 95% ethyl alcohol; it did not dissolve in water, ether, acetone, benzene, dichloroethane, chloroform, or carbon tetrachloride. The colorless crystals, purified with alcohol and kept over sulfuric acid, fused at 190-191°C (with decomposition).

0.1640 g substance:	8.49 ml N/10 solution of Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> .
0.1591 g substance:	8.20 ml N/10 solution Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> .
5.005 mg substance:	2.896 mg BaSO <sub>4</sub> .
5.501 mg substance:	3.187 mg BaSO <sub>4</sub> .

3.200 mg substance: 4.380 mg CO<sub>2</sub>; 1.012 mg H<sub>2</sub>O.  
 2.760 mg substance: 3.786 mg CO<sub>2</sub>; 0.882 mg H<sub>2</sub>O.  
 2.880 mg substance: 0.186 ml N<sub>2</sub> (24°C, 743 mm).  
 3.470 mg substance: 0.224 ml N<sub>2</sub> (20°C 737 mm).

Found %: As 19.41, 19.34; S 7.96, 8.04; C 37.33, 37.40;  
 H 3.53, 3.58; N 7.26, 7.29.

C<sub>12</sub>H<sub>13</sub>N<sub>2</sub>SAAsO<sub>6</sub>. Calculated %: As 19.33; S 8.25; C 37.11; H 3.25; N 7.22.

### 3. Preparation of 3,3-p-diaminobenzosulfamido-4,4-dihydroxy-arsenobenzene (III)

This compound was prepared by the reduction of aminobenzosulfanilamido-dihydroxy-arsinic acid by sodium hydrosulfite. 10 g of the sodium salt of this acid were dissolved in 300 ml of water. The solution was heated over a water bath in a flask equipped with a mechanical stirrer. Finely powdered sodium hydrosulfite (120 g) was gradually added in small portions to the solution, heated to 55°C. A precipitate slowly settled out of the solution as the hydrosulfite was added. After the reaction mixture had cooled the precipitate was isolated by filtering. After washing on the filter with water and chilled alcohol, the precipitate was dried in a vacuum desiccator at 50-55°C. Yield: 9.4 g. To purify it the product was placed in a Soxhlet apparatus and extracted with alcohol. The alcohol extract was decanted into 20 volumes of water. Slight acidulation with an aqueous solution of hydrochloric acid precipitated a white deposit, which was filtered, and washed with water and alcohol. The dry product weighed 6.7 g. The substance fused at 180-181°C (with decomposition) and was insoluble in water, isopropyl, butyl, or amyl alcohols, ether, benzene, toluene, carbon tetrachloride, acetic acid, mineral acids, and ammonia. Analysis of the preparation yielded the following results:

0.1572 g substance: 9.2 ml N/10 solution Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>.  
 0.1488 g substance: 8.7 ml N/10 solution Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>.  
 5.625 mg substance: 3.775 mg BaSO<sub>4</sub>.  
 4.905 mg substance: 3.250 mg BaSO<sub>4</sub>.  
 2.848 mg substance: 4.450 mg CO<sub>2</sub>; 0.858 mg H<sub>2</sub>O.  
 3.292 mg substance: 5.150 mg CO<sub>2</sub>; 1.056 mg H<sub>2</sub>O.  
 4.585 mg substance: 0.313 ml N<sub>2</sub> (19°C, 751.5 mm).  
 5.580 mg substance: 0.410 ml N<sub>2</sub> (23°C, 730 mm).

Found %: As 21.95, 21.92; S 9.21, 9.10; C 42.61, 42.66;  
 H 3.37, 3.59; N 7.93, 8.02.

C<sub>24</sub>H<sub>22</sub>N<sub>4</sub>S<sub>2</sub>As<sub>2</sub>O<sub>6</sub>. Calculated %: As 22.18; S 9.47; C 42.6; H 3.24; N 8.28.

### 4. Preparation of the Sulfanilamido-hydroxy-phenylarsenoxide (V)..

Sulfur dioxide (from a tank) was passed through a solution of 10 g of aminobenzene-sulfanilamido-hydroxyarsinic acid in 300 ml of hydrochloric acid (sp. gr. 1.19) at a temperature of 10-12°C. at a speed of 85-90 bubbles per minute for 2 hours and 45 minutes. As reduction proceeded, the dark brown solution was gradually decolorized. At the end of the reaction, a white precipitate settled out of the transparent solution. After 50 ml of concentrated hydrochloric acid had been added to the reaction solution and the latter had been chilled, the precipitate was filtered out. The hydrochloride salt of amino-benzene-sulfanilamido-hydroxy-arsenoxide was purified easily and did not decompose in storage. Upon recrystallization from alcohol it had a m.p. of 162-163°C. The colorless crystals dissolved easily in water and alcohol. The hydrochloride salt was dissolved in water to prepare the aminobenzene-sulfanilamido-hydroxy-arsenoxide (VI) The solution was neutralized with 10% solution of soda. The resulting colorless crystals were recrystallized from 86% alcohol and then had a m.p. of 135-136°C (with decomposition). Upon exposure to air the substance turned pink. It was soluble in water, alcohol, and acetone, but insoluble in ether or benzene.

0.1680 g substance: 8.7 ml N/10 solution Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>.  
 0.1775 g substance: 9.2 ml N/10 solution Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>.  
 3.128 mg substance: 1.893 mg BaSO<sub>4</sub>.  
 4.422 mg substance: 2.652 mg BaSO<sub>4</sub>.  
 5.680 mg substance: 2.111 mg AgCl.  
 3.402 mg substance: 4.593 mg CO<sub>2</sub>; 1.001 mg H<sub>2</sub>O.  
 2.229 mg substance: 3.956 mg CO<sub>2</sub>; 0.852 mg H<sub>2</sub>O.  
 3.560 mg substance: 0.224 ml N<sub>2</sub> (27°C, 737 mm).  
 5.935 mg substance: 0.383 ml N<sub>2</sub> (27°C, 729 mm).

Found %: As 19.41, 19.43; S 8.08, 8.23; Cl 9.29; C 36.84, 36.76;  
 H 3.29, 3.28; N 7.09, 7.07.

C<sub>12</sub>H<sub>12</sub>N<sub>2</sub>ClSAsO<sub>4</sub>. Calculated %: As 19.20; S 8.19; Cl 9.09; C 36.87; H 3.09; N 7.17.

### 5. Preparation of 3,3-p-diacetobenzene-sulfamido-4,4-dihydroxy-arsenobenzene (VI).

A solution of 18 g of the hydrochloride salt of diamino-3,3-dihydroxy-4,4-arsenobenzene in 400 ml of water was placed in a flask equipped with a mechanical stirrer. Acetanilide sulfochloride (37.5 g), recrystallized from dichloroethane, was added in small portions to the solution, heated on a water bath to 40°C. As this was done the color of the flask contents gradually turned from dark to light yellow. The reaction lasted 3 hours 30 minutes. Toward the end of the reaction a slight, pale yellowish precipitate was deposited. After cooling the precipitate was filtered out and successively washed upon the filter with hot water, alcohol, and ether. The preparation was treated with dichloroethane, then with alcohol, and lastly with ether, in order to eliminate the unreacted acetanilide sulfochloride. The substance (17.3 g), dried over sulfuric acid in an exsiccator, fused at 230-231°C (with decomposition). Under the action of weak acids and bases the product saponifies easily, even at ordinary temperatures. The small, colorless, flocculent crystals turned yellow upon prolonged exposure to the air. The preparation dissolved in water, alcohol, ether, acetone, and benzene; it was only slightly soluble in dilute hydrochloric acid (with saponification of the acetyl group).

0.1750 g substance: 9.15 ml N/10 solution  $\text{Na}_2\text{S}_2\text{O}_3$ .  
 0.1906 g substance: 10.0 ml N/10 solution  $\text{Na}_2\text{S}_2\text{O}_3$ .  
 4.395 mg substance: 2.645 mg  $\text{BaSO}_4$ .  
 3.470 mg substance: 2.096 mg  $\text{BaSO}_4$ .  
 0.2184 g substance: 5.91 ml N/10 solution  $\text{NaOH}$ .  
 0.2456 g substance: 6.44 ml N/10 solution  $\text{NaOH}$ .  
 3.659 mg substance: 5.973 mg  $\text{CO}_2$ ; 1.221 mg  $\text{H}_2\text{O}$ .  
 3.432 mg substance: 5.604 mg  $\text{CO}_2$ ; 1.196 mg  $\text{H}_2\text{O}$ .  
 5.910 mg substance: 0.382 ml  $\text{N}_2$  (27°C, 725 mm).  
 6.040 mg substance: 0.387 ml  $\text{H}_2$  (26°C, 729 mm).

Found %: As 19.6, 19.67; S 8.26, 8.30;  $(\text{CH}_3\text{CO})$  11.63, 11.56;  
 C 44.56, 44.53; H 3.75, 3.90; N 7.00, 7.05.

$\text{C}_{26}\text{H}_{23}\text{N}_4\text{S}_2\text{As}_2\text{O}_9$ . Calculated %: As 19.75; S 8.42;  $(\text{CH}_3\text{CO})$  11.31; C 44.21; H 3.42; N 7.37.

### 6. Reaction of 3,3-p-diaminobenzesulfamido-4,4-dihydroxy-arsenobenzene (III) with rongalite.

The calculated quantity of rongalite was added in small portions to a solution of 10 g of the substance in 100 ml of dilute (1:5) hydrochloric acid. The transparent solution grew cloudy as the first portions of rongalite were added. Further addition of rongalite caused the deposition of a pale yellow precipitate. At a temperature of 50-60°C the reaction lasted 2 hours 35 minutes. After the reaction was over the reaction mixture was chilled. The deposited precipitate was filtered out and successively washed on the filter with dilute (1:5) hydrochloric acid, water, alcohol, and, finally, ether. Yield: 4.2 g. The pale yellow crystals, fusing at 246-248°C (with decomposition), were insoluble in water, alcohol, ether, benzene, carbon tetrachloride, acetone, and toluene; slightly soluble in alkalis and mineral acids. The quantitative determination of arsenic and sulfur yielded the following results:

0.1540 g substance: 7.95 ml N/10 solution  $\text{Na}_2\text{S}_2\text{O}_3$ .  
 0.1971 g substance: 10.2 ml N/10 solution  $\text{Na}_2\text{S}_2\text{O}_3$ .  
 0.2800 g substance: 0.2554 g  $\text{BaSO}_4$ .  
 0.1956 g substance: 0.1788 g  $\text{BaSO}_4$ .  
 Found %: As 19.56, 19.41; S 12.54, 12.73.

$\text{C}_{26}\text{H}_{23}\text{N}_4\text{S}_3\text{As}_2\text{O}_9\text{Na}$ . Calculated %: As 19.33; S 12.38.

### CONCLUSIONS

1. The reaction of acetanilide-benzene sulfochloride with amino-3-hydroxy-4-phenylarsinic acid proceeds smoothly, forming acetosulfanilamido-hydroxy-phenylarsinic acid, which is easily saponified by hydrochloric acid with the formation of sulfanilamido-hydroxy-phenylarsinic acid.
2. The compound prepared is easily reduced by sodium hydrosulfite to the corresponding arseno compound, and by sulfurous acid to the sulfanilamido-phenylarsenoxide. In both cases the reduction involves the saponification of the acetyl group.
3. The synthesized preparations were tested for their trypanocidal, spirocheticidal, streptococcic, and pneumococcic chemotherapeutic activity.

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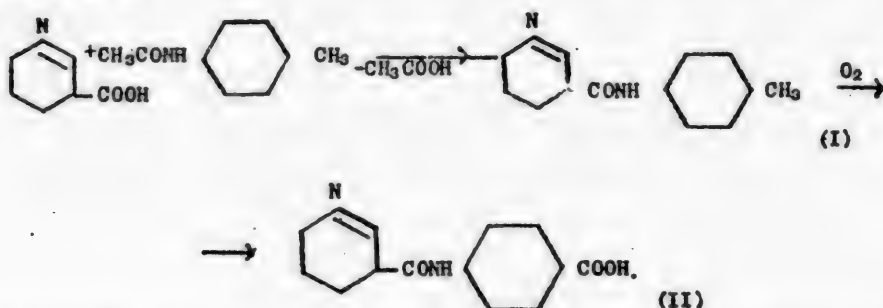


# N-NICOTINOYL-P-AMINOBENZOIC ACID

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A new derivative of p-aminobenzoic acid, with the nicotinoyl radical in the amino group, has been prepared. The synthesis of the preparation was effected in accordance with the following diagram:



The p-toluide of nicotinic acid (I) was prepared by fusing p-acetotoluidine with nicotinic acid. Substitution of the acetic acid by nicotinic acid begins at 150-160°C; the process is most intensive at 250-260°C, at which temperature some of the nicotinic acid sublimes. The reaction product is chilled and treated with weak hydrochloric acid. The nicotinic acid and its toluidine are converted into a solution. After the p-acetotoluidine has been filtered out, the solution is alkalinized and thus freed from the unreacted nicotinic acid; nicotinoyl-p-toluide is in the precipitate. The p-toluide of nicotinic acid is oxidized by potassium permanganate in a neutral medium:

The preparation is insoluble in water or organic solvents. Its insolubility in organic solvents and its high melting point (293-294°C) resembles those of the biogenic amino acids.

## EXPERIMENTAL

1. p-Toluide of nicotinic acid (I). A mixture of 12 g (0.1 mole) of nicotinic acid and 17 g of p-acetotoluidine (the latter in excess), which has been carefully prepared in advance, is placed in a 100-ml long-necked, round-bottomed flask. The flask is placed in a Babo funnel, and the temperature of the mass is raised to 250-260°C during half an hour. This temperature is then maintained for another half an hour, during which time all the acetic acid is driven off. After this the reaction mass is allowed to cool off gradually for half an hour, falling to, say, 40°C. Thus the entire process lasts about one hour and a half. The cooled reaction mass is treated two or three times with 3% hydrochloric acid; the acid solution is filtered; the precipitate contains about 4 g of the unreacted p-acetotoluide. The acid filtrate is neutralized with soda or ammonia. This causes about 13 g of the p-toluide of nicotinic acid to precipitate out

of the solution. The technical product is washed with water, dried, and then recrystallized from boiling water (1:200). 12 g of the purified preparation is obtained in the form of long shining needles. M.p. 146-147°C. Yield: 58% in terms of nicotinic acid (only traces of nicotinic acid can be obtained from alkaline solutions).

2. N-nicotinoyl-p-aminobenzoic acid (II). 0.3 liter of water are placed in a half liter flask equipped with a mechanical stirrer and a thermometer. In this water, while the stirrer is operating, there are dissolved 15 g of magnesium sulfate, and 13 g of the purified p-toluide of nicotinic acid are added. The mixture is heated to 75°C for three hours, and 35 g of potassium permanganate are added in small batches. The temperature within the flask is maintained in the 72-80°C range. After all the potassium permanganate has been added, the stirring and heating are continued for another hour. The hot solution is then filtered. The alkaline filtrate is carefully neutralized with hydrochloric acid, throwing down nicotinoyl-p-aminobenzoic acid. Yield: 8 g. The manganese peroxide is treated three times with boiling water, 250 ml of water being used the first time, and 125 ml being used for the third treatment. From these wash waters some 2 g of the unoxidized para toluide of nicotinic acid are crystallized.

The nicotinoyl-p-aminobenzoic acid is dissolved in a 10% solution of crystalline soda, the resulting solution being boiled with activated charcoal for 30 minutes. The solution is filtered, and the filtrate carefully acidulated with dilute hydrochloric acid. From 8 g of the technical product we obtain 7 g of the pure preparation. Yield: 80%. M.P. 293-294°C.

4.051 mg substance: 0.401 ml N<sub>2</sub> (14.5°C, 746 mm).

3.347 mg substance: 0.332 ml N<sub>2</sub> (15°C, 747 mm).

Found %: N 11.55, 11.57.

C<sub>13</sub>H<sub>10</sub>O<sub>3</sub>N<sub>2</sub>. Calculated %: N 11.57.

#### CONCLUSIONS

A new derivative of p-aminobenzoic acid, with the nicotinoyl radical in the amino group: N-nicotinoyl-p-aminobenzoic acid, has been prepared by the oxidation of the para toluide of nicotinic acid.

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# INVESTIGATIONS OF POLYCYCLIC COMPOUNDS

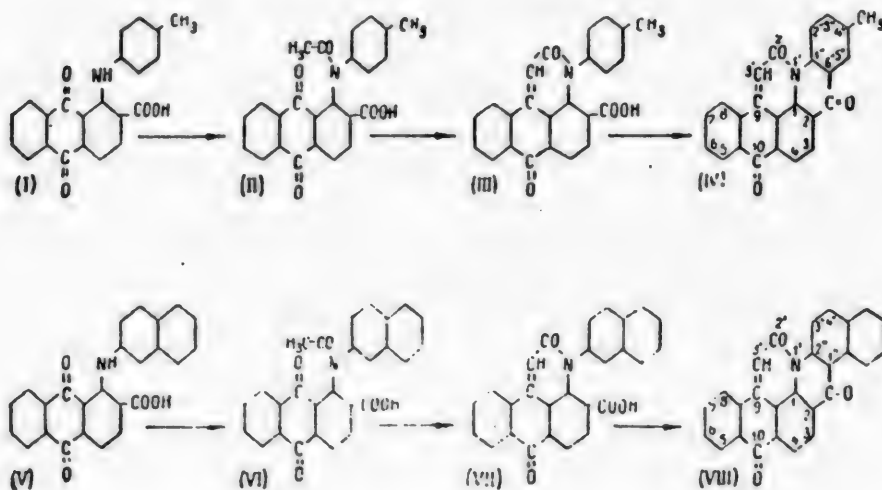
## IX. SYNTHESIS OF METHYL- AND BENZANTHRAPYRIDONE-ACRIDONES

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In our first communication we described the synthesis and some of the properties of 1-(N)-9-anthrapyridone-1,1''-phenylene-2,6''-ketone, abbreviated as anthrapyridone-acridone. [1] With a view to the further study of this class of compounds we have recently prepared 1-(N)-9-anthrapyridone-1,1''-(p-tolylene)-2,6''-ketone (IV) and 1-(N)-9-anthrapyridone-1,2''-(β-naphthylene)-2,1''-ketone (VIII). For the sake of simplicity, we shall henceforth call the first of these latter compounds methyl-anthrapyridone-acridone, and the second, benzanthrapyridone-acridone.

The synthesis of these substances was effected in the manner previously described:



The initial substances for these syntheses -- 1-aryldoanthraquinone-2-carboxylic acids -- were previously prepared by the condensation of the corresponding amine with anthraquinone-1-chloro-2-carboxylic acid. At the present time the synthesis of anthraquinone-1-aryldo-2-carboxylic acid has been greatly simplified by utilizing the brief specifications of German Patent 237,236 [2], on the possibility of condensing aromatic amines with anthraquinone 1-nitro-2-carboxylic acid and the corresponding data on the

condensation of the same acid with p-aminobenzoic acid.

The properties of the methyl- and benz-anthrapyridone-acridones were found to be analogous to those of the simplest anthrapyridone-acridone. The change in vat color that is so characteristic of the latter is likewise found in its homologues. Thus, a solution of the sodium salt of the leuco compound of methyl-anthrapyridone-acridone is violet, quickly changing to brown, exactly as is the case with anthrapyridone-acridone. The sodium salt of the leuco compound of benzanthrapyridone-acridone first forms a cornflower-blue solution. Upon standing (for 15-20 minutes) this color also turns brown.

The subject of this communication is a more detailed study of the changes that occur when an alkaline solution of sodium hydrosulfite acts upon anthrapyridone-acridone and its homologues.

#### EXPERIMENTAL

**Anthraquinone-1-(p-tolyl)-2-carboxylic acid (I).** A suspension of 5 g of magnesium oxide in 100 ml of distilled water is boiled for 15 minutes, after which 8.5 g of soda, 10 g of p-toluidine, and 10 g of anthraquinone-1-nitro-2-carboxylic acid are added, and the whole boiled for 15 hours, with constant stirring. The reaction mass is filtered, and the sodium salt of tolylamino-carboxylic acid is extracted from the precipitate with boiling water. The bulk filtrate is combined with the extracts, and after acidulation of the violet-colored solution the free acid separates out as a violet precipitate. The yield is 11.2 g (97% of theoretical). After crystallization from glacial acetic acid it fuses at 275-276°C (uncorrected) (according to the literature the m.p. is 276.5-276°C, uncorrected).

**Anthraquinone-1-(N)-acetyl-tolylamino-2-carboxylic acid (II).** 10 g of tolylamino-anthraquinone carboxylic acid (I) are boiled for 10 minutes with 20 ml of acetic anhydride and 30 ml of glacial acetic acid. The brown solution obtained is poured into 250 ml of water. The yellow precipitate formed is filtered after cooling, washed with water and dried. The yield is 10.6 g (95% of theoretical). The substance is obtained in pure form, as yellow needles, by successive recrystallization from 80% acetic acid and butyl alcohol. A solution in sulfuric acid is likewise yellow-colored. It fuses with decomposition at about 300°C.

3.535 mg substance: 0.105 ml  $N_2$  (22°C, 764 mm).

6.059 mg substance: 0.188 ml  $N_2$  (22°C, 764 mm).

Found %: N 3.46, 3.61.

$C_{24}H_{17}O_5N$ . Calculated %: N 3.57.

**1-(N)-9-anthrapyridone-N-tolyl-2-carboxylic acid (III).** 5 g of the crude acetyl derivative (II) are dissolved in 250 ml of an 0.8% solution of caustic soda and boiled for 10 hours. The brown solution, which possesses an intense green fluorescence, is filtered from the slight insoluble residue and acidulated with hydrochloric acid. The yield is 4.6 g (96% of theoretical). The substance is obtained in the form of bright yellow, thin little crystals by successive recrystallization from glacial acetic acid and butyl alcohol. It melts with decomposition at about 320°C. A solution in sulfuric acid is yellow in color.

6.775 mg substance: 0.211 ml  $N_2$  (24°C, 763 mm).

5.170 mg substance: 0.169 ml  $N_2$  (23°C, 763 mm).

Found %: N 3.59, 3.79.

$C_{24}H_{15}O_4N$ . Calculated %: N 3.67.

**Methyl-anthrapyridone-acridone (IV).** 5 g of recrystallized anthrapyridone carboxylic acid (III) are added to 25 ml of chlorosulfonic acid and heated at 40-45°C for 2 hours. The red solution is decanted on 200 g of ice. The yellow deposit that settles out is filtered and washed with water. The yield is 4.7 g (98% of theoretical). The substance is purified by crystallization from ortho dichlorobenzene and xylene. m.p. 354-355°C. It forms a red solution with sulfuric acid.



4.646 mg substance: 0.138 ml N<sub>2</sub> (13°C, 737 mm).  
4.873 mg substance: 0.174 ml N<sub>2</sub> (20°C, 738 mm).  
Found %: N 3.93, 4.04.  
C<sub>24</sub>H<sub>15</sub>O<sub>3</sub>N. Calculated %: N 3.85.

When an alkaline solution of sodium hydrosulfite acts upon methyl-anthrapyridone-acridone at room temperature it produces a dark-violet vat color. After a short while (15-20 minutes), but almost instantaneously when heated, the color changes, turning brown.

When cotton cloth is dipped into the violet solution it is dyed violet, changing upon oxidation into a yellow that is fast to the action of dilute acids. In the brown solution the cloth is dyed brown, changing to orange upon oxidation. Dilute acid turns the cloth yellow, alkali turns it orange again.

Anthraquinone-1-( $\beta$ -naphthylamino)-2-carboxylic acid (V). A suspension of 5 g of magnesium oxide in 100 ml of distilled water is boiled for 15 minutes, after which 8.5 g of soda, 11 g of  $\beta$ -naphthylamine, and 10 g of anthraquinone-1-nitro-2-carboxylic acid are added, and the whole boiled, with constant stirring, for 15 hours. An excess of hydrochloric acid is then added to the suspension, which is stirred for 1 hour, and the bluish-violet deposit filtered out and washed. The yield is 12.7 g (96% of theoretical).

After recrystallization from glacial acetic acid, substance (V) fuses at 259-260°C (corrected) (the m.p. is given as 261.5°C, corrected, in the literature).

Anthraquinone-1-(N)-acetyl-( $\beta$ -naphthylamino)-2-carboxylic acid (VI). 10 g of the unpurified naphthylamino-carboxylic acid (V) are stirred into 50 ml of glacial acetic acid and 10 ml of acetic anhydride and heated for 30 minutes over a boiling water bath. The brown solution obtained is poured, together with the yellow precipitate, into 50 ml of water. After cooling, the precipitate is filtered out, washed with water, and dried. The yield is 10.5 g (95% of theoretical). Yellow needles are obtained by crystallization from acetic acid and then from butyl alcohol. When heated to 170-180°C, substance (VI) is converted into anthraquinone-benzacridone.

7.150 mg substance: 0.196 ml N<sub>2</sub> (18°C, 754 mm).  
6.170 mg substance: 0.174 ml N<sub>2</sub> (21°C, 753 mm).  
Found %: N 3.19, 3.28.  
C<sub>27</sub>H<sub>17</sub>O<sub>3</sub>N. Calculated %: N 3.22.

1-(N)-9-anthrapyridone-N-( $\beta$ -naphthyl)-2-carboxylic acid (VII). 10 g of substance (VI) are dissolved in 400 ml of an 0.8% solution of caustic soda and boiled for 10 hours. The hot solution is filtered and acidulated. The brown deposit that is precipitated out is filtered and washed with water. The yield is 9 g (94% of theoretical). After twofold crystallization from butyl alcohol the substance is in the form of light-brown needles. M.p. 324-325°C.

6.005 mg substance: 0.177 ml N<sub>2</sub> (19°C, 761 mm).  
8.660 mg substance: 0.253 ml N<sub>2</sub> (20°C, 756 mm).  
Found %: N 3.44, 3.39.  
C<sub>27</sub>H<sub>15</sub>O<sub>4</sub>N. Calculated %: N 3.35.

Benzanthrapyridone-acridone (VIII). 5 g of the recrystallized carboxylic acid (VII) are added to 75 ml of concentrated sulfuric acid and stirred for 1 hour at room temperature. The cherry-red solution is poured into 300 ml of water. The brown deposit that settles is filtered out and washed with water. The yield is 4.35 g (91% of theoretical). The substance is insoluble in nitrobenzene, o-dichlorobenzene, and glacial acetic acid, and almost insoluble in pyridine, naphthalene, and phenol. The substance could not be purified by crystallization from organic solvents owing to its low solubility. It was purified by repeated dissolution in concentrated sulfuric acid and diluting the filtered solution with an equal volume of 80% acetic acid. It fuses at 360°C.

6.380 mg substance: 0.188 ml N<sub>2</sub> (17°C, 762 mm).  
8.010 mg substance: 0.243 ml N<sub>2</sub> (19°C, 748 mm).  
Found %: H 3.47, 3.49.  
C<sub>27</sub>H<sub>15</sub>O<sub>3</sub>N. Calculated %: N 3.57.

A blue vat color is formed by the action of an alkaline solution of sodium hydrosulfite. The color of the solution soon takes on a green tinge, subsequently turning orange-brown. Cotton cloth is dyed blue by the blue vat color, turning yellow after oxidation. Upon being dipped into the orange-brown solution the cloth is dyed orange, the color remaining unchanged upon oxidation, merely turning brighter. The action of acid causes the color to turn yellow.

#### CONCLUSIONS

1. Two homologues of anthrapyridone-acridone: methyl- and benz- anthrapyridone-acridone, have been synthesized.

2. The properties of the substances produced are analogous to those of the simplest anthrapyridone-acridone.

3. Introducing the pyridone chain into the molecule of methyl- and benz- anthraquinone-acridones produces a marked hypsochromic effect, as is the case with the simplest anthraquinone-acridone.

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## INVESTIGATIONS OF POLYCYCLIC COMPOUNDS

### X. ACTION OF ALKALIS ON ANTHRAPHYRIDONE-ACRIDONES

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In our previous communications we described the syntheses of anthrapyridone-acridone (I) [1], methyl-anthrapyridone-acridone (II) and benzanthrapyridone-acridone (III) [2]. Under the action of an alkaline solution of sodium hydrosulfite these compounds first form normal reduction products, easily changing back to the initial substance upon oxidation. Upon standing for a short time (15-20 minutes at room temperature or 2-3 minutes at 60°C), the initial color of a sodium salt solution of the leuco compound [violet for (I) and (II), and blue for (III)] changes, turning brown. When the brown solutions are oxidized by atmospheric oxygen, no precipitate separates out, as might have been expected in ordinary leuco compounds. Substances that differ sharply from the initial compounds can be separated out by acidifying the solution.

In our further research we found, using anthrapyridone-acridone as a model, that this substance can be prepared by simply heating anthrapyridone-acridone with an alkaline solution (in this case the reaction also takes place in the cold, but quite slowly). This fact indicates that the final conversion of anthrapyridone-acridone is effected by the alkali, and not by the hydrosulfite. The presence of sodium hydrosulfite facilitates the reaction, probably because of the circumstance that anthrapyridone-acridone is not in suspension, but in a sodium-salt solution of its leuco form (IV). The solubility of the substances prepared, not only in caustic alkalis, but also in carbonates and bicarbonates of the alkali metals, most likely indicates the presence in it of carboxylic groups. Titration of the alkali, performed conductometrically, indicated that 2 moles of alkali are required for 1 mole of the carboxylic acid (V).

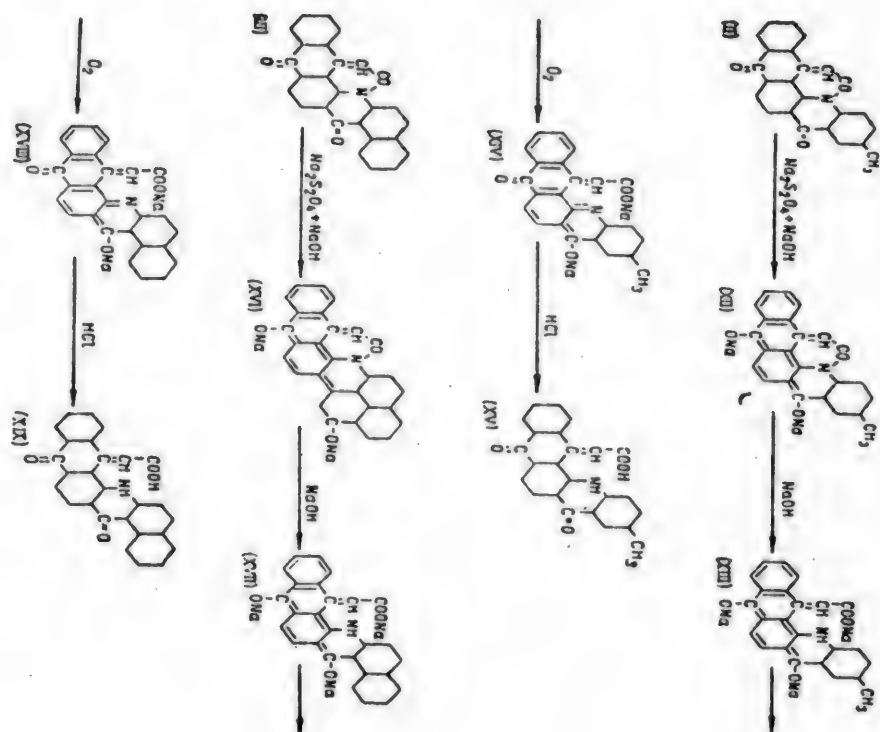
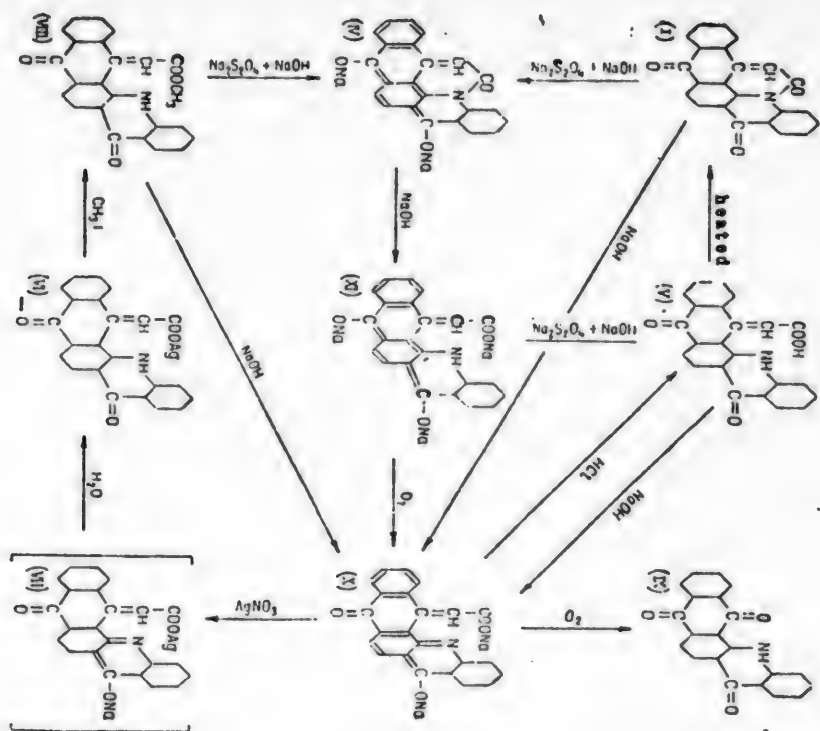
Salts (V) of the alkali and alkali-earth metals dissolve easily in water, coloring it an intense orange. The silver, copper (Cu<sup>++</sup>), and lead (Pb<sup>++</sup>) salts are only slightly soluble in water. One molecule of the silver salt (VI) contains, according to analysis, one atom of silver, and thus, obviously, is obtained by the hydrolysis of the silver-sodium salt (VII). We were unable to isolate the latter compound. The methyl ester (VIII) was prepared by the action of methyl iodide upon (VI).

Endeavors to split the carboxyl groups from (V) proved fruitless, as the carboxylic acid (V) is stabilized upon direct heating or upon heating in mixtures with oxides of the alkali-earth metals, as well as in anhydrous organic-solvent media, easily splitting off a molecule of water and forming (I). We likewise failed to isolate the acid chloride: (I) was obtained when thionyl chloride acted upon (V). (V) is likewise converted into (I) by heating it slightly in concentrated sulfuric acid or by letting it react with chlorosulfonic acid at room temperature.

The alkali salts of the carboxylic acid (V) oxidize extremely easily. The oxidation reaction takes place even with atmospheric oxygen at room temperature. Anthraquinone-acridone (IX) was isolated as the oxidation product.

Our experimental data justify the assumption that when alkalis act upon anthrapyridone-acridone the pyridine ring is opened while the acridone group is enolized ( $I \rightarrow X$ ). Under the action of a mineral acid the free 9-methylene-anthrone-acridone-9-carboxylic acid (V) is liberated.

To explain the consumption of 2 moles of alkali per mole of acid (V), we assumed that an enol form of the acridone ring was formed.





The absence of analogical tautomeric conversion for (IX) may be due to the hydrogen bond between the nitrogen of the acridone ring, and the carbonyl group of the anthraquinone ring. It is quite probable that such a bond exists, analogous to the structure of anthraquinone-1,2,2',1'-dihydrazine<sup>[2]</sup>.

The action of alkalis on (II) and (III) likewise result in the formation of the corresponding carboxylic acids, which leads us to believe that this reaction is general for the whole series of anthrapyridone-acridones. We found no mention in the literature of analogous opening of the pyridone ring under the influence of alkalis in other classes of compounds.

In conclusion we wish to acknowledge our indebtedness to Academician A. E. Porai-Koshits for the advice and encouragement given us in carrying out this research.

#### EXPERIMENTAL

##### Preparation of 9-Methylene-Anthrone-Acridone-9-Carboxylic Acid. (V).

a) By the action of an alkaline solution of sodium hydrosulfite. 5 g of (I), reprecipitated from sulfuric acid, are mixed with 50 ml of a 10% solution of caustic soda and diluted with 2 liters of water, after which 20 g of sodium hydrosulfite is added. Cotton cloth dipped into the dark-violet solution of the sodium salt of the leuco compound (IV) is dyed violet. When drops of acid are applied to the cloth, the color turns yellow (the color of the free leuco compound). Upon oxidation in the air the cloth takes on a lemon-yellow color, which resists the action of dilute acids. Solution (IV) is allowed to stand for 1 hour, with periodic shaking; this causes all of (IV) to convert into (XI). Cotton cloth dipped into the brown solution (XI) is dyed brown. When a drop of acid is applied the color turns pinkish-yellow (the color of the free leuco compound). Oxidation in the air changes the brown color of the cloth to a pure orange, which turns yellow [formation of (V)] when acted on by dilute acids. Dilute alkalis again turn the cloth orange ( $V \rightarrow X$ ).

The brown solution is filtered, and the filtrate is acidulated with hydrochloric acid. The brown precipitate that settles out is filtered out, washed, and purified by triple precipitation from a solution of sodium bicarbonate. 4.1 g of a light yellow powder is obtained, representing 75% of the theoretically possible quantity.

b) By the action of a base. A suspension of 3 g of (I) in 25 ml of a 10% solution of caustic soda is allowed to stand for 48 hours at room temperature, after which it is filtered, the filtrate acidulated, and the precipitate (V) purified as above. The yield is 0.66 g (21% of theoretical). When the suspension, comprising exactly the same quantities of its constituents as before, is boiled for an hour, the yield of (V) equals 2.6 g (82% of the theoretical).

If a 1:1 water-alcohol solution of caustic soda is used instead of an aqueous solution, the reaction is completed after 5 minutes of boiling. Yield: 84.6% of the theoretical.

The acid (V) is insoluble in water, soluble with difficulty in alcohols, and somewhat more soluble in acetic acid and dioxane. The solutions are colored yellow; the acid is insoluble in aromatic hydrocarbons (benzene, toluene, xylol), dichlorobenzene, or nitrobenzene. It dissolves in caustic alkalis and the carbonates and bicarbonates of the alkali metals, the solutions being an intense orange. Its solution in concentrated sulfuric acid is orange red in color. Small, light yellow needles are obtained by triple recrystallization from 80% acetic acid. Upon heating to approximately 270°C (V) is converted, without fusion, into (I). A brown solution (XI) is formed by the action of an alkaline solution of sodium hydrosulfite. The dyeing of cotton by this solution has been described above. A suspension of (V) in dilute acetic acid dyes wool yellow. This dye is not fast to alkalis.

3.279 mg substance: 9.015 mg CO<sub>2</sub>; 1.339 mg H<sub>2</sub>O.

2.702 mg substance: 7.409 mg CO<sub>2</sub>; 1.055 mg H<sub>2</sub>O.

2.888 mg substance: 0.108 ml N<sub>2</sub>; (20°C, 731 mm).

4.921 mg substance: 0.162 ml N<sub>2</sub>; (25°C, 728 mm).

Found %: C 74.98; 74.78; H 4.57; 4.37; N 3.99; 4.18.  
C<sub>23</sub>H<sub>13</sub>O<sub>4</sub>N. Calculated %: C 75.19; H 4.57; N 3.81.

2.0 mg substance: 35.0 mg camphor:  $\Delta t$  8.5° (by the Rasta method).  
 3.1 mg substance: 39.6 mg camphor:  $\Delta t$  9.0° (by the Rasta method).  
 1.8 mg substance: 27.8 mg camphor:  $\Delta t$  7.0° (by the Rasta method).

Found: N 351, 397, 369.  
 $C_{23}H_{13}O_4N$ . Calculated: M 367.34.

**Titration.** To a weighed portion of (V), mixed with 50 ml of water, there are added 13.6 ml of N/10 NaOH. Titration is done conductometrically with a N/10 solution of HCl. The results of titration are shown in the figure and listed in the table below.

**Sodium salt (X).** One g of (V) is dissolved with heating in 15 ml of a 3% solution of caustic soda, and 2 g of sodium chloride are added. When the dark-brown solution is cooled, small yellow needles (X), grouped in clusters, separate out. Substance (X) was not obtained in a pure state, without traces of NaCl. When we endeavored to crystallize it from methanol, we obtained (I).

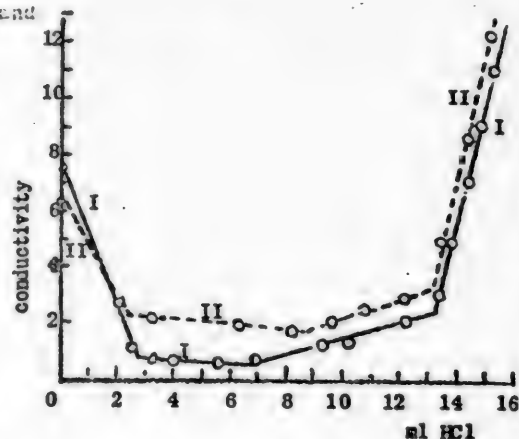
**Silver salt (VI).** 1.84 g (0.005 mole) of the carboxylic acid (V) are dissolved in 0.75 g (0.009 mole) of the sodium bicarbonate and 60 ml of water. The solution is then filtered to remove excess acid (V); the filtrate is cooled, and a solution of 1.7 g (0.01 mole) of silver nitrate is added. The solution is filtered, daylight being excluded, and the precipitate is washed with water, methanol, and ether. The yield of (V) is 2.05 g (96.2% of theoretical). The yellow powder obtained is hardly soluble at all in water and soluble with difficulty in alcohols; it turns darker when exposed to light.

**Analysis:** A weighed portion of (VI) is boiled for 30 minutes with 10 ml of 25% nitric acid, after which it is filtered and washed. Hydrochloric acid is added to the filtrate. The deposit of silver nitrate is collected on a weighed glass filter, washed, and dried.

0.1178 g substance: 0.0362 g AgCl.  
 0.1994 g substance: 0.0608 g AgCl.  
 Found %: Ag 23.14, 22.96

$C_{23}H_{12}O_4NAg$ . Calculated: Ag 22.8.

**Methyl ester (VIII).** 2.37 g (0.005 mole) of the freshly prepared silver salt (VI) are mixed with 7.1 g (0.05 mole) of methyl iodide and boiled for 1 hour. The excess  $CH_3I$  is driven off in vacuum, and the ester (VIII) is extracted with 300 ml of 70% acetic acid. Upon cooling 1.2 g of a precipitate settles out. M.p 198-202°C. The precipitate is dissolved in benzene and purified by chromatographic adsorption on  $Al_2O_3$ . Evaporation of the benzene solution yields 0.6 g of (VIII). It is obtained as greenish yellow elongated hexagonal crystals (from acetone). It is soluble in most organic solvents, turning them yellow. M.p. 206-206.5°C.



Quantity	Number ml of HCl required for neutralization		
	Excess of NaOH	Sodium salt (X)	Total
200 mg .....	2.7	10.5	13.2
200 mg .....	2.4	10.8	13.2
$C_{23}H_{14}O_4NNa_2$ . Calculated	2.7	10.9	13.6

It dissolves without change in concentrated sulfuric acid, forming an orange-colored solution. When heated with a 1% solution of caustic soda, it saponifies, turning into (X).

An alkaline solution of sodium hydrosulfite does not react with (VIII) at room temperature; upon heating it causes the ring to open, forming (IV)

3.647 mg substance: 10.082 mg CO<sub>2</sub>; 1.518 mg H<sub>2</sub>O.  
5.109 mg substance: 14.136 mg CO<sub>2</sub>; 2.179 mg H<sub>2</sub>O.  
8.007 mg substance: 0.263 ml N<sub>2</sub> (19°C, 733 mm).  
5.441 mg substance: 0.191 ml N<sub>2</sub> (23°C, 739 mm).  
Found %: C 75.39, 75.46; H 4.65, 4.77; N 3.70, 3.93.  
C<sub>24</sub>H<sub>16</sub>O<sub>4</sub>N. Calculated %: C 75.58; H 3.96; N 3.67.

#### Oxidation of (V) in an alkaline medium.

a) By atmospheric oxygen. 0.5 g of (V) is dissolved in 20 ml of a 10% solution of caustic soda, and air containing no CO<sub>2</sub> is allowed to pass through the solution for 4 hours at room temperature. The violet deposit formed (IX) is filtered out, washed, and dried. Yield: 0.15 g (30% of theoretical). Further passage of air through the filtrate results in practically complete oxidation of (V) to (IX). At 100°C the oxidation reaction is twice as rapid.

b) By potassium permanganate. 0.37 g (0.001 mole) of (V) is dissolved in 20 ml (0.002 mole) of N/10 KOH and 50 ml of water. The solution is heated to boiling, and a solution of 0.8 g (0.005 mole) of KMnO<sub>4</sub> in 15 ml of water is gradually added. The solution is then cooled and filtered, and the precipitate is treated with dilute sulfuric acid and sodium bisulfite. After filtering and washing, we obtain 0.24 g of (IX) (74% of theoretical). It is crystallized in the form of violet needles, with a m.p. of 381-383°C, from o-dichlorobenzene. A test mixture with anthraquinone-acridone produced no depression.

6.99 mg substance: 0.259 ml N<sub>2</sub> (22°C, 749 mm).  
Found %: N 4.22.  
C<sub>21</sub>H<sub>11</sub>O<sub>3</sub>N. Calculated %: N 4.38.

#### Preparation of 9-Methylene-Anthrone-4-Methyl-Acridone-9-Carboxylic Acid (XV).

5 g of (II), freshly precipitated from sulfuric acid, are mixed with 50 ml of a 10% solution of caustic soda, 2 liters of water, and 20 g. of sodium hydrosulfite. A violet solution (XII) is formed, which dyes cotton cloth violet, the color turning to yellow upon oxidation. The color of the solution changes after the lapse of 20-30 minutes, turning brown (formation of XIV). When acted upon by dilute acids, the orange color of the cloth is changed to yellow (the color of the free acid XV). After standing for an hour, the brown solution is filtered and the filtrate is acidulated with hydrochloric acid. The brown deposit (XV) that settles out is purified by reprecipitation from a solution of sodium bicarbonate. The yield is 4 g (76% of theoretical).

The carboxylic acid (XV) is soluble in alkalis and in the carbonates and bicarbonates of the alkali metals, the solutions having an intense orange color. A solution in concentrated sulfuric acid is red in color. Upon heating the substance is converted to (II) without fusion. A test mixture with (II) produces no depression; its m.p. is 352-254°C.

#### Preparation of 9-Methylene-Anthrone-Benzacridone-9-Carboxylic Acid (XIX)

Benz-anthrapyridone-acridone (III) is treated with an alkaline solution of sodium hydrosulfite as described above. A cornflower-blue solution (XVI) is formed. The color rapidly changes, turning brown (formation of XVII). Acidulation of solution (XVII) causes the carboxylic acid (XIX) to separate out. After purification the acid is obtained in the form of a light-brown powder. The acid is soluble in solutions of alkalis and of the carbonates and bicarbonates of the alkali metals, forming orange-colored solutions; its solution in concentrated sulfuric acid is red in color.

#### CONCLUSIONS

1. It has been found that the action of an alkali (especially easily in the presence of sodium hydrosulfite) causes the pyridone ring in anthrapyridone-acridone to open, forming the 9-methylene-anthrone-acridone-9-carboxylic acid.

2. The structure of this acid is confirmed by all its properties, in particular, by its reconversion into anthrapyridone-acridone and the formation of anthraquinone-acridone upon its oxidation.

3. It has been demonstrated that the reaction of opening the pyridone ring under the influence of an alkali is a general phenomenon for the anthrapyridone-acridone series.

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